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A STUDY OF THE KINETICS OF THE MERCURY REACTION WITH THE SILVER-TIN DENTAL ALLOYS

A THESIS

Presented to

The Faculty of the Graduate Division

by

John Wayne Koger

In Partial Fulfillment

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A STUDY OF THE KINETICS OF THE MERCURY REACTION WITH THE SILVER-TIN DENTAL ALLOYS

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SUMMARY

The rate of the reaction of mercury with the silver-tin dental alloy (copper and zinc present in trace amounts) to form dental amalgam was studied. The purposes of this research were to determine what factors affect the reaction rate, the magnitude of the effect of these factors on the reaction rate, and the mechanism of the reaction.

The principal method of investigation involved the use of x-ray diffraction to observe the amalgamation reaction. Different types of commercial alloys and some partially processed alloys were reacted with chemically pure mercury. Condensation and trituration time were held constant for all samples.

In general, the results showed that the surface area or particle size and the processing through which an alloy was carried affect the reaction rate, with the processing being the more important factor, considering alloy composition essentially constant. Increased cold-work of the alloy particles decreased the total time of reaction. The percent of the total reaction that takes place during trituration was determined for all alloys with varying amounts of mercury. The percent of mercury that would react during trituration, regardless of the amount present, was evaluated and found to be constant for each alloy. The total time of reaction for all alloys with varying amounts of mercury was determined. It was also determined that from the reaction rate standpoint, the Eames Technique produced a satisfactory amalgam.

CHAPTER I

INTRODUCTION

The term "dental amalgam" refers to the alloy silver-tin-mercury-(copper-zinc in trace amounts) which is used as the primary restorative material for tooth structure. Dental amalgam is made by mechanically mixing a silver-tin-(copper-zinc) alloy with mercury. The resulting plastic mass is immediately forced into the prepared tooth cavity and allowed to harden. The mixing of the alloy and the mercury, known as trituration, is done by a mortar and pestle or a mechanical amalgamator. The product of the trituration is a plastic mass and the forcing of the mass into a cavity is known as condensation. Condensation often results (sometimes purposely) in squeezing mercury out of the preparation.

The American Dental Association Specification for Dental Amalgam Alloys gives the following requirements in regard to the composition of the alloy:

Silver	65%	minimum
Tin	29%	maximum
Copper	6%	maximum
Zinc	2%	maximum
Mercury	3%	maximum (before amalgamation)

Silver, the main component, imparts high strength, rapid hardening, and high expansion in amalgam.

Tin reduces the expansion or increases the contraction, causes slow setting, and decreases the strength and hardness.

Copper replaces the silver and is similar to it with regard to

expansion. Copper hardens the amalgam and increases its flow resistance.

Zinc will combine with impurities that might be present and protect the other metals.

The study of the reaction between the mercury and the alloy is of vital importance to the dentist. The reaction rate will determine how fast the dentist must work in filling the cavity and the total reaction time will determine what care the patient must take after the work is finished. There are a number of other physical properties which are important and which the dentist must consider; however, this work involves only the reaction rates and total time of reaction.

The present work was undertaken because there has been little work done in determining what factors, such as particle processing and particle size, affect the initial reaction during trituration and the rate of reaction after trituration. Also no investigations have been carried out to determine what causes the differences in the rate of reaction between different commercial alloys and mercury when particle size, condensation, and trituration time is held constant.

The purposes of this work were to determine what factors affect the reaction rate, the magnitude of the effect of these factors on the reaction rate, and the mechanism of the reaction.

This was accomplished by triturating the alloy and mercury, condensing the plastic mass into a special specimen holder and then immediately placing the plastic mass in an x-ray diffractometer and observing the changes occurring as hardening took place. Condensation and trituration time were held constant for all samples. The variation in peak intensity of the various phases versus time gave an indication of the reaction rate and the actual reaction taking place.

CHAPTER II

SURVEY OF PREVIOUS WORK

Earliest Work

Amalgam has a history of over one hundred years. In 1895 Black (1) presented the first reliable information concerning the composition, manufacturing, and testing of physical properties of amalgam. He was also responsible for the balanced alloy (in which he counteracted the expansion of one element with the contraction of another) and information on its manipulation.

The first equation proposed for the amalgamation reaction was:

$$Ag_3Sn + Hg \rightarrow Ag_3Hg_4 + Sn$$

This was formulated by McBain and Joyner (2) in 1912.

The next studies of the setting reaction of dental amalgams by Knight and Joyner (3), Gray (4), Gaylor (5), Troiano (6), and Stenbeck (7) determined that the reaction involved the formation of the silver-mercury and tin-mercury phases.

Systems of the Phases Formed in Amalgamation Reaction

Table 1 gives the phases referred to and their composition. In the usual convention, no subscript refers to the silver-tin phase, subscript 1 refers to the silver-mercury phase and subscript 2 refers to the tin-

Table 1. Composition of Phases in Dental Amalgam

Phase	Composition	
γ	25-27.5% Sn - Balance Ag;	Ag_3Sn
β_1	60% Hg - 40% Ag ;	AgHg
γ_1	70% Hg - 30% Ag ;	Ag_2Hg_3
δ_2	about 35% Hg - Balance Sn (disputed)	
γ_2	9 - 18% Hg - Balance Sn -- considered in this work and in calculations as Sn_8Hg	

mercury phase. The Greek letters refer to the specific phase (β, γ, etc.) in the corresponding phase diagram. The phase diagrams of the above systems are given in Figures 1, 2, and 3.

The systems involved in the amalgamation reaction have been studied in detail by several people. Using x-ray methods, Murphy (11) was the first to investigate the silver-mercury system. Later Preston (12) and Stenbeck (7) also investigated this system, as did Winterhager and Dreiner (13) in very recent work. According to Murphy and Preston, the β_1 phase and γ_1 phase did occur at room temperature. Stenbeck gave a = 2.964 Å and c = 4.831 Å for the β_1 phase, a hexagonal structure. Winterhager and Dreiner gave a = 10.013 Å for the γ_1 phase, a cubic structure. Confusion has existed as to whether the silver-mercury phase is Ag_3Hg_4 (Murphy and Preston), Ag_2Hg_3 (identified by Ryge and co-workers, given as Moschallandsbergite in the ASTM index), or Ag_5Hg_8 (Stenbeck). Ag_2Hg_3 is generally accepted as being correct. The phase diagram is given in Figure 1.

Fairhurst and Ryge (14) investigated the tin-mercury phase of dental amalgam using x-ray diffraction techniques and reported the characteristic d-values and intensities. Taylor and Burns (9) redetermined the mercury-tin system and found it to be more complicated than previously reported. Their phase diagram is given in Figure 2.

The phase diagram of the silver-tin system is given in Figure 3. As was earlier stated, it was found that the most desirable composition for the dental restorative alloy was in the Ag_3Sn phase, region (γ).

Studies of the Amalgamation Reaction and the Reaction Rate

Gaylor proposed that the reaction took place by β_1 and γ_2 first

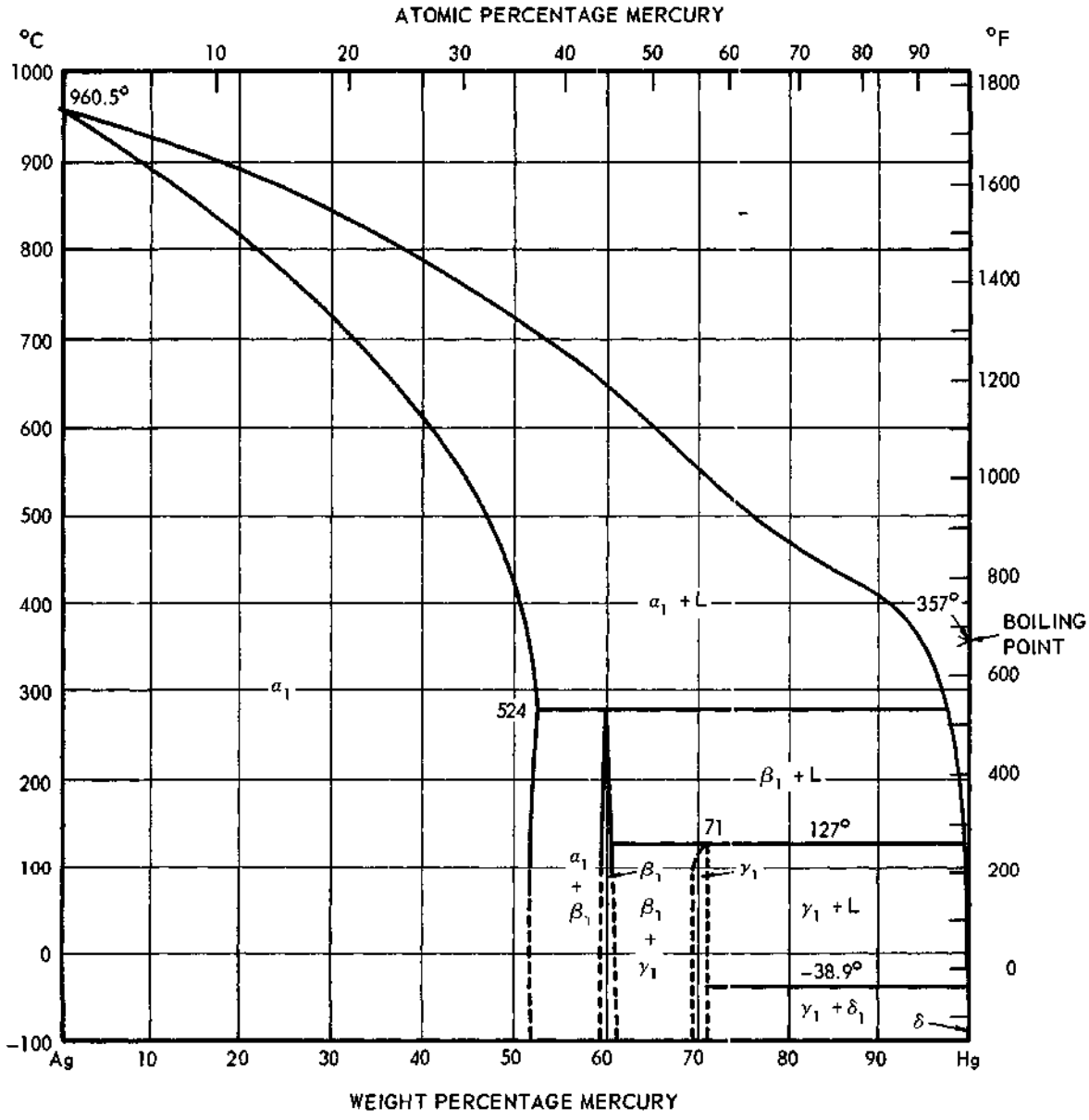

Figure 1. Silver-Mercury Phase Diagram (8).

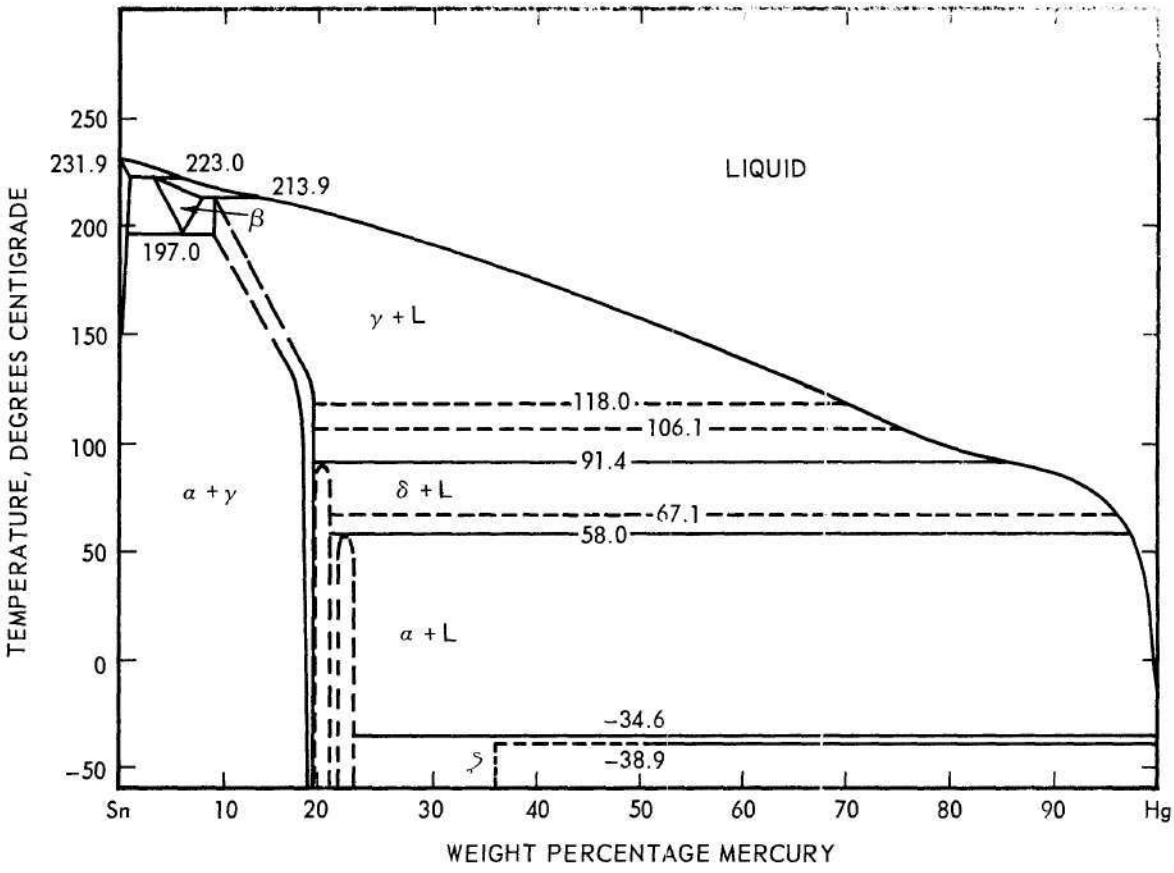

Figure 2. Tin-Mercury Phase Diagram (9).

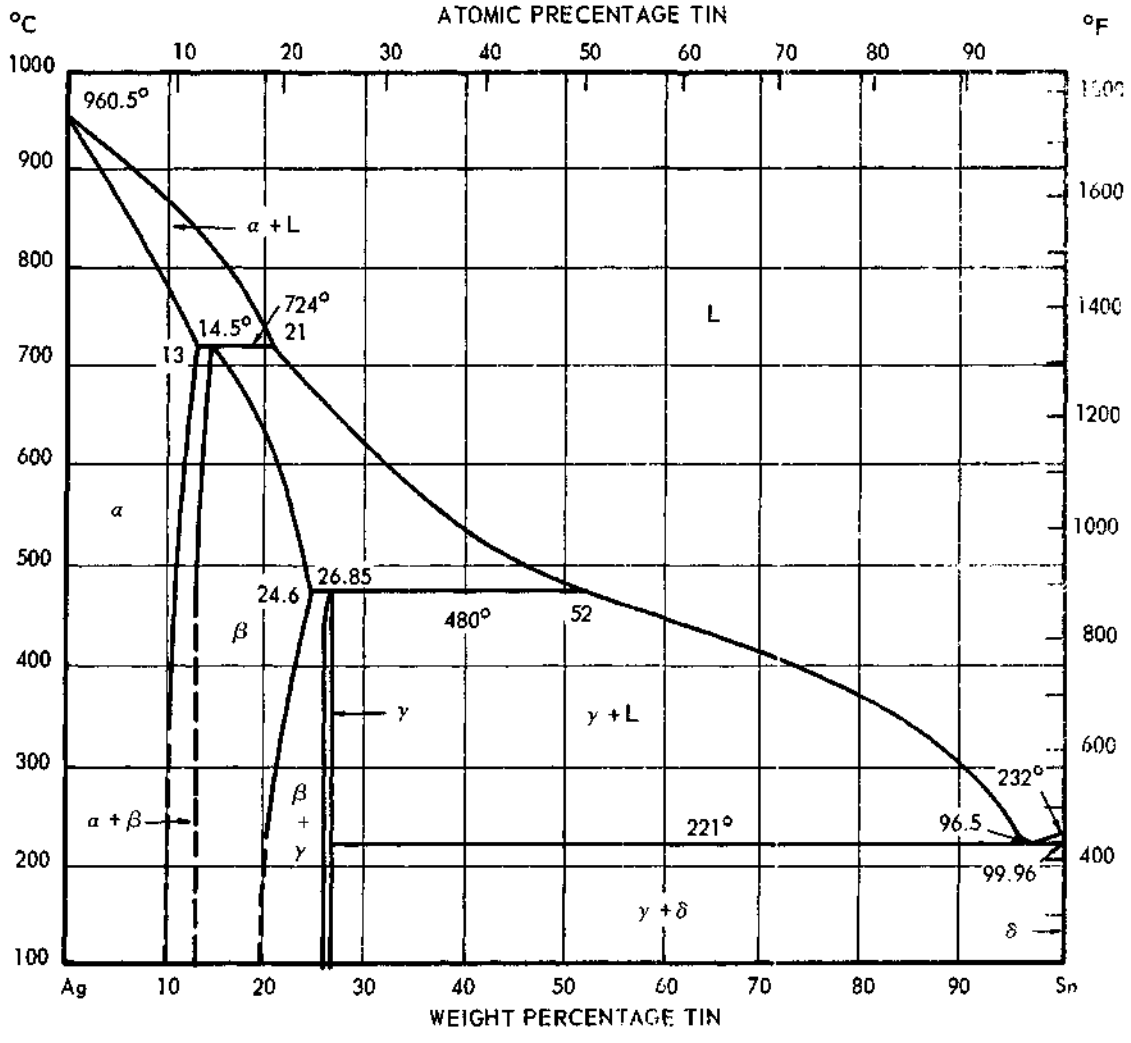

Figure 3. Silver-Tin Phase Diagram (10).

being formed and then going to $\beta_1 + \gamma_1 + \gamma_2$. She explained the expansion of the dental amalgam by the presence of β_1 and γ_1 phase and explained the contraction by the presence of free Sn plus Ag_3Sn.

Troiano proposed that γ_1 and δ_2 and unattacked Ag_3Sn were first formed, went to $\gamma_1 + \gamma_2$, and then went to $\gamma_1 + \gamma_2 + \beta_1$. Troiano suggested that dendritic growth caused the expansion as holes occurred. Contraction was then due to the precipitation of the δ_2 phase in the γ_1 dendrites and therefore reduction of the holes.

These theories have both been the subject of much discussion since their formulation in the 1930's. Ryge and co-workers (15), Fairhurst (14), Dreiner (16), and Wainwright (17) have all disputed the existence of the δ_2 phase.

The latest and most generally accepted idea is that as the alloy is mixed with mercury during trituration, the Ag_3Sn compound dissolves or absorbs mercury and two crystalline phases, γ_1 and γ_2, result. γ_1 precipitates first, but γ_2 grows faster. Ryge, Fairhurst, and Fischer (18) express the reaction as

$$Ag_3Sn + Sn + Hg \rightarrow Ag_2Hg_3 + (Sn, Hg) + \underset{\text{(unreacted)}}{Ag_3Sn}$$

Ryge, Moffett, and Barkow (15) were the first to investigate the phase formation versus the time of the amalgamation reaction. They also investigated the rate of formation of the phases as influenced by the mercury-alloy ratio, particle size, and trituration time. They found that the removal of unreacted mercury immediately after the trituration cuts

down the rate of formation and the final intensity of the phases that form, particularly that of the γ_2 phase.

Winterhager and Dreiner (13) investigated the reaction of silver and mercury, tin and mercury, and silver-tin and mercury using the methods of x-ray diffraction. In their study of the silver-tin and mercury reaction, they studied the effect of varying silver content as sometimes 50% silver alloys are used for the dental amalgam alloy in Europe. They also studied the effect of particle size, the effect of mercury content, the influence of trituration time and the influence of mechanical compacting methods.

Mitchell, Schoonover, Dickson, and Vacher (19) froze amalgams and used x-ray diffraction techniques to study the phases present. They established that the liquid mercury vanishes at the time of greatest dimensional changes. They also attributed the initial shrinkage as being due to the formation of phases having small volume. They then explained that expansion resulted from the diffusion of unreacted mercury into new alloy particles, and later, additional phases of smaller volume than the starting materials occur again and are responsible for the last slight contraction.

Alloy Powder Manufacture

In the general manufacturing process of Ag_3Sn alloy, metals of good purity must be used, alloying must take place without oxidation or incorporation of any impurities, and casting must be done with care to prevent oxidation and incorporation of impurities. The ingot is usually cast in the form of a cylinder and cut into filings with the proper equipment,

usually some type of lathe. Some inferior alloys are considered complete after this step. However, on cooling, coring will take place. Heating to about 425° C. for twenty-four hours before cutting into filings will usually homogenize the alloy. In good alloys, the bar is now cut into filings which are heat treated to remove the stresses put in by cold-work.

Because of the cold-work of the particles, freshly cut filings amalgamate much faster than filings that have been aged for several months at room temperature and the hardening amalgam often expands considerably. An aging effect which will eliminate cold-work can be attained by heating the filings for thirty minutes in boiling water. If aged filings are used, less mercury is required for trituration and slightly less mercury is retained in the hardened amalgam after condensation. Properties of hardened amalgam made with aged filings are less effected by technic variation. This amalgam has greater cohesiveness during condensation, the amalgam is stronger and has less flow, and the amalgam has less tendency to expand excessively.

Particle size is about the greatest single difference in the alloys available. Other factors being equal, a smaller particle size produces more rapid hardening of the amalgam with greater strength than do the larger alloy particles because of the larger available surface area.

One brand of alloy (20), whose manufacturing process is known, is made by alloying the pure metals at 2,100° F. in an oxygen-free atmosphere. After casting, the alloy is cut into filings on special lathes to achieve the particle size desired. The powder is graded by screening on rotary sieves and the desired mesh sizes blended. The powder is then annealed for eight hours at 100° C. to eliminate internal stresses and to give the

alloy an exact setting period. The powder is then double washed.

Spherical Alloy Particles

Some recent research has been done using spherical alloy particles as opposed to the randomly shaped particles. Demaree and Taylor (21) prepared different size range spherical alloy particles and determined physical properties on amalgam specimens made from individual size ranges, mixtures of size ranges, and commercial allcys. For the spherical alloys, an increase in particle size increased the amount of expansion during setting, and the length of time needed to attain final set decreased the residual mercury content. The particle size had no significant effect on flow after hardening had been completed. Particles 15 - 30 microns in diameter gave the maximum strength, and all particle sizes under 50 microns gave high early strength. They found that the advantages of spherical alloys over conventional-type alloys were good control of physical properties by suitable blending of particle sizes, less sensitivity to manipulation variables, less flow, higher early compressive strength, and simplification of the manipulation process.

Waterstrat and Hicho (22), using x-ray techniques, showed that spherical alloy particles are strain free. They also showed that the internal deformation of cold-worked regular alloy particles could be removed by heating at a high temperature or during the reaction when mercury is added.

Physical Properties Studies

In discussing the background work with regard to physical properties of amalgams, it is desired to present the more important observations

and the work that includes compilation of the latest available data. No attempt will be made to give all the background work on physical properties of amalgams.

Properties which are the most important to amalgams are dimensional stability, strength, and flow. A dental amalgam may either expand or contract during solidification and will flow or "creep" under very light loads. The strength of the amalgam can be measured as compressive, tensile, or transverse strength. The properties will be discussed separately and the factors contributing to the properties will be given.

Dimensional Changes

The following conditions will cause the amalgam to expand (at times excessively): too high a silver content (over 75%), more than 5% copper, moisture coming in contact with the zinc, unaged filings, and manipulation to favor the formation of the γ_1 and γ_2 phases. The following conditions will cause the amalgam to contract: too high a tin content, manipulation to decrease the formation of the γ_1 and γ_2 phases, very long time of trituration, increased pressure in condensation, and a small particle size.

Mitchell and his co-workers (19) observed that amalgams showed less expansion when they were prepared at 21° C. and maintained at 37° C. (98.6° F.--body temperature) than when they were prepared and maintained at 21° C. Peterson and Oaks (23) showed that amalgams which solidify at 37° C. have less setting expansion than amalgams which solidify at 25° C. Some amalgams manipulated according to manufacturer's directions show a contraction within twenty-four hours at 37° C. and would not meet specifications at this temperature.

Fusayama, Shimyu, Hosoda, and Horibe (24) measured transverse and early amalgam expansion and correlated residual mercury content and hardness with differences in dimensional change. They found much initial contraction during the first ten minutes and associated high mercury content with the highest hardness.

Crowell and Phillips (25) showed that as the surface area of the particles increases, expansion and setting time decreases.

Wing (26) showed that increasing the amount of mercury available initially (over that recommended) increases the dimensional change. Lowering the mercury content decreased expansion and perhaps caused contraction. It was also shown that an increased amount of trituration and a decrease in particle size reduced expansion. Ward and Scott (27) observed that increased condensation decreased the expansion.

Compressive Strength

Under or over trituration will affect the strength of the amalgam; and the longer the time between trituration and condensation, the greater the loss in strength. Usually, higher condensation pressure gives greater compressive strength while lowering the mercury content. With respect to strength, a mercury content of 45 - 53% is desirable.

Eames, Skinner, and Mizera (28) conducted tests on "dry" (50% or less mercury at the beginning) amalgams to see the comparison (strength values) with the usual "wet" mix a dentist uses. It was shown that lightly condensed amalgam specimens containing 50% mercury and from which no excess mercury was removed had high crushing strength. They compared favorably with specimens condensed under pressure with excess mercury removed during condensation. Thirty seconds of trituration resulted in a

drier mix and higher crushing strength than fifteen seconds of trituration. Specimens permitted to harden for three minutes before condensing in two minutes were well within acceptable strength ranges. Consistently better condensed and stronger amalgam restorations resulted from a 50% mercury mix than from a much dryer one.

Overberger, Povlich, and Sausen (29) showed trituration effect on strength. Increased mechanical amalgamation caused a significant increase in the one hour strength to a maximum and then a decrease. Miller (30) had earlier shown the need for high crushing strength in the first hour to prevent early fracture. Increased mechanical amalgamation caused no significant increase in the 24 hour and seven day strengths which display relatively constant strengths that gradually decrease. The relative particle thickness did not seem to be a controlling factor for the strengths of the amalgams tested. It was found that trituration must be thorough to impart adequate strength and decreased trituration should be avoided to prevent loss in strength.

Caul, Longton, Sweeney, and Paffenbarger (31) showed the effects of rate loading, time of trituration, and test temperature on compressive strength. Compressive strength was higher on machines that applied a constant stress rate than on those applying a constant strain rate when the testing time was greater than one minute. Compressive strength at 60° C. was 50% of its strength at 23° C. The optimum time for triturating each amalgam on the basis of strength was taken as the minimum time to develop maximum compressive strength.

Peyton and Liatkus (32) showed how the compressive strength of amalgam is influenced by different condensation forces. Poor condensation

affected strength and low condensation force affected one hour strength most. Fine particle alloy amalgam did not necessarily mean high compressive strength. It was also found that, when well condensed, an amalgam with low mercury content did not necessarily develop its maximum strength faster than one with a higher mercury content. Crowell and Phillips (25) showed that compressive strength increases as the surface area of the alloy particle increases. One hour strength showed the greatest amount of increase.

Wing (26) showed that amalgams made with fine-grained alloys show higher early compressive strength and higher final compressive strength. It was also shown that increasing the amount of mercury available initially (over that recommended) lowered the compressive strength. Decreasing the amount of mercury increased the early strength and setting rate. It also was noted that an increased amount of trituration increased the compressive strength. No relationship was found between flow and compressive strength.

Tensile Strength

Rodriguez and Dickson (33) did the most nearly complete work in the tensile strength determinations of amalgams. They prepared miniature tensile test specimens and showed that varying the head speed made no difference in the tensile strength of week-old specimens. One hour old amalgams attained only 10 - 15% of the tensile strength attained in one week, about 7,000 - 8,000 psi. Tensile strength was about 1/5 to 1/4 of their compressive strength. Coy and Liebig (34) showed that tensile strength was greater with a fine-cut alloy after one day, but all were about the same after five days.

Transverse Strength (Bending Strength)

Mahler and Mitchem (35) evaluated the transverse strength and compared it to the compressive and tensile strength. Compressive, tensile, and transverse strength decreased as residual mercury increased. All strengths showed the same sort of curve in this respect. It was also found that rate of loading did not influence transverse or tensile strength but did affect compressive strength.

Flow (Creep)

Flow is increased with increasing temperature and is decreased with an increase in condensation. Skinner (36) showed that the flow of amalgam was about twice as great at 37° C. as at room temperature. Peterson and Oaks (23) showed that amalgams which solidify at 37° C. had greater flow than amalgams which solidify at 25° C.

Wing (26) observed that increasing the amount of mercury available initially (over that recommended) increased the flow.

Crowell and Phillips (25) showed that as the surface area of the alloy particle increases, flow decreases.

Summary of Previous Work

Numerous investigations have been concerned with the amalgamation reaction. The phases formed during the reaction have been identified and their role in affecting dimensional changes, strength, and flow have been studied. There has also been investigation to determine phase formation versus time as influenced by the mercury-alloy ratio, particle size, and trituration time.

No investigations have been carried out to determine what factors,

such as particle processing and particle size and shape, affect the initial reaction during trituration and the rate of reaction after trituration. Also, no investigations have been carried out to determine what causes the differences in the rate of reaction between different commercial alloys and mercury when particle size, condensation, and trituration time is held constant.

This work was undertaken to study these effects.

CHAPTER III

EXPERIMENTAL PROCEDURE

Sample Preparation

Weighed portions of alloy and mercury were placed together in a glass mortar and triturated with a glass pestle. A "pen grip" was used so that the pressure of the pestle on the mortar was about two pounds. A minimum trituration time was used for each alloy and percent mercury mixed, to determine the dependency of the trituration time on the type alloy. The mixture was triturated until five seconds after no free mercury could be seen. A special specimen holder of plexiglass had been constructed, and the plastic mass was condensed into the back side of the holder against a glass slide to insure that the sample would be flat when placed in the x-ray diffraction unit. In condensation, care was taken to express no free mercury. After all of the plastic mass was condensed into the specimen holder, or after about 90 seconds (whichever came first), the holder was placed into the x-ray unit. Each step was timed until the sample was placed in the x-ray unit after which the chart paper kept a record of the time.

The total weight of each amalgam specimen was from five to ten grams. In this study each alloy was mixed with 20, 30, 40, 50, and 60% mercury. Also, for each commercial alloy sample, a 60% mercury amalgam was made and squeezed with a cotton squeeze cloth before being condensed into the specimen holder and put in the x-ray unit.

Materials Used

Some of the alloys used were of commercial variety and were purchased on the open market. One group of alloy powders was furnished by a manufacturer after different steps in the manfacturing process. A bar of Ag_3Sn was obtained from an alloy manufacturer, turned on a lathe to obtain powder, and this powder was used with no other treatment. Table 2 gives a description of all the alloy powders used.

The mercury used was bought from a dental supply house and is the type used by dentists. The mortar and pestle and condensors used were also standard dental equipment.

X-Ray Diffraction Work

The x-ray diffraction work was done on a Phillips High Angle Goniometer Diffractometer using Cu Kα radiation and a Ni filter. The x-ray unit operated at 50 KV and 40 MA using a proportional counter with a pulse height analyzer to eliminate unwanted radiation and with a 1° divergence slit, a 6 mil receiving slit, and a 1° scatter slit.

After determining the d-spacings for each phase included in the dental amalgam, it was seen that at least two major peaks of each phase were found between 28° 2θ and 43° 2θ. Therefore, the x-ray unit was made to oscillate continuously from 28° to 43°, from 43° to 28°, etc., for each sample. The total time each sample was allowed to react depended on the alloy and the mercury present. No runs of longer than eight hours were made because of growth of the amalgam and complications concerning the geometry of the system. In x-ray diffraction work, the surface of the specimen must remain level at all times. The scanning speed in most

Table 2. Alloys Used and Their Description

Alloy	Description
Commercial	
J	Fine grained alloy
K	Regular grained alloy
M	Fine grained alloy
N	Only alloy made by this company
O	Only alloy made by this company
Experimental	
A	Cast ingot, annealed at 400° C., slow cooled, made into filings, filings not annealed
B	Cast ingot, made into filings, filings annealed
C	Cast ingot, annealed at 400° C., slow cooled, made into filings, filings annealed
D	Cast ingot, made into filings, filings not annealed
L	Cast ingot, heat treated for 72 hours at 720° F. and 24 hours at 510° F., made into filings, filings not annealed
Spherical	Received from R. M. Waterstrat, National Bureau of Standards

cases was 2° per minute; however, in some cases the speed was decreased to 1/2° per minute to see if any d-spacing changes could be determined.

In this investigation, condensation was held constant for all samples. Each sample was triturated to the same point, i.e., until five seconds after the time which no free mercury could be seen. Under these conditions, the factors affecting the reaction rates may be lessened so closer examination may be given to the other more significant factors.

CHAPTER IV

DISCUSSION OF RESULTS

The x-ray diffraction observation of the mercury-silver-tin-(copper-zinc) reaction permitted the determination of the amount of reaction that took place during trituration (the initial mixing of the mercury and the alloy), the reaction rate after trituration, and the total time of reaction. From these results, the factors that affect the reaction rates and the total time were determined. Also from the observations of the reaction, the characteristic lines and intensities of the phases that make up the dental amalgam were found and reported. As a result of this work, an equation for the amalgamation reaction is given and a quantitative analysis scheme that could be applied to this work is proposed.

Treatment of Data

After a run was completed, the height of each peak was taken and the time of its occurrence recorded. Line heights, measured in impulses per second, serve as criterion for the intensity. This is only permissible if the width of the intensity at half-height does not change with time, and if there is a sharp reflection. These conditions were present in this work. The intensity of the largest peak of each phase was taken, divided by the largest intensity found (usually the $2\theta = 38.0^{\circ}$ line, Ag_2Hg_3 phase at t_∞) multiplied by 100, and plotted versus the time at which it occurred. This normalization of the time dependent intensities

of the major peak of the Ag_2Hg_3 phase eliminates the effect of surface dimension changes on the intensity and possible growth textures on hardening and permits agreement between two like experiments.

Line of greatest intensity °2θ (Cu Kα radiation)	Planes	Phases
38.0	330,411	Ag_2Hg_3
39.6	111,021	$Ag_3Sn(Hg)$*
32.2	100	Sn_8Hg

*Unreacted mercury in solid solution in the Ag_3Sn.

Typical graphs for one alloy with varying amounts of mercury used in reaction are given in Figures A-1, A-2, A-3, A-4, A-5, and A-6. The individual points obtained are not plotted on the graphs.

Figures A-7, A-8, and A-9 show typical intensities of the diffraction peaks at certain times as they are recorded on the x-ray diffraction chart paper.

It was seen that the intensity of the major Ag_2Hg_3 peak versus time plots satisfied the curve

$$It = I_\infty(1 - e^{-bt^n})$$

(used by Winterhager and Dreiner (13) in their studies of reaction rates) where:

t = time

I_t = intensity at time t

I_∞ = maximum intensity attained

$$\text{at } t = 0,\ I_t = 0$$

$$\text{at } t = \infty,\ I_t = I_\infty$$

When the log of the equation is taken twice, the following equation results:

$$\log \log I_\infty/(I_\infty - I_t) = b \log e + n \log t$$

$$\text{let } k = b \log e$$

A plot of log $I_\infty/(I_\infty - I_t)$ versus t on log-log paper gives a straight line of slope n and y-intercept of k or b log e. These plots are given for all alloys and amounts of mercury used in Figures A-10 to A-21. (The individual points obtained are not plotted on the graphs.) The value of b gives an indication of the amount of Ag_2Hg_3 formed during trituration or the amount of mercury reacted during trituration. The value of n gives an indication of the rate of reaction after trituration. From the latter equation, an expression for the half-life, $t_{1/2}$, is obtained.

$$t_{1/2}{}^n = \ln 2/b$$

experimentally, $I_{t\infty/2}$ occurs at $t_{1/2}$.

From these equations, it is seen that the half-life can be found experimentally by observing at what time the intensity is found to be one-half the maximum intensity and can be calculated using the n and b values to check the reliability of the results. The experimental and calculated half-lives were found to be very close.

Results

It is seen from data discussed later that the amount of reaction that takes place during trituration is dependent on the amount the alloy has been processed. The order of increased processing,

D (unannealed filings made from cast ingot),

B (annealed filings made from cast ingot),

A (unannealed filings made from homogenized ingot),

C (annealed filings made from homogenized ingot),

is the order of decreasing b value or percent total reaction that takes place during trituration for almost all mercury percentages used. This order of increased processing is also the increasing order of total mercury that will react during trituration, regardless of the amount of mercury present, and is the order of increasing n values or reaction rate after trituration. The order of increased processing is also the order of increasing half-lives and increasing necessary trituration time. The total reaction time does not follow the processing order and will be discussed later.

It is seen from the lists that compare the various values that results for alloy L amalgams usually are in the center for the amalgams made with experimental alloys. Alloy L, by actual treatment, was heat treated in the ingot stage by the manufacturer and cut into filings in this work and should respond to amalgamation about like alloy A, not considering particle size differences. It did react as expected.

An x-ray diffraction pattern was run on the powders of the four alloys, A, B, C, D, that were each removed from the manufacturing process at a different point, to compare the widths at half-heights of the intensities.

It was found, as expected, that the unannealed powders had the broadest widths. In order of decreasing broadness, the results were A, D, C, and B. This should also be the order of decreasing amounts of cold-work within the particles.

It is seen that this order of decreased cold-work is the order of increased total reaction time in most of the specimens.

The alloys processed in different stages have about the same particle size and surface area; so, the variations in b, n, half-life, total reaction time, and trituration time are due to incomplete processing and cold-work of the alloy powders. Alloy C is actually not partially processed as it was taken through the complete sequence of processing. Therefore, the values of b, n, etc., for the amalgams made with commercial alloys are compared to these same values for the amalgams made with alloys A, B, C, and D, especially C.

The amalgams that have the largest b values, the smallest n values and smallest half-lives should have the greatest surface area or smallest particle size if all are fully processed. It follows that the amalgams with the smallest b values, largest n values, and largest half-lives should have the smallest surface area or largest particle size. On this basis, in comparing the b, n, and half-life values of all the assumed completely processed commercial alloys, it is seen that this order should prevail:

alloy	particle size	surface area
M	smallest	largest
K		
O		
spher.		
N		
J		
C	largest	smallest

If this is not the true order of sizes as may be seen by the actual measurement, Table 8, then the different degrees of processing may be the reason. (The tables of results will follow this order of alloys.)

Alloys M, K, O, and spherical have decreasing surface areas and increasing particle size as do alloys N, J, and C. From their properties and the fact that alloy C is known to have gone through a full cycle of manufacturing steps, alloys N, J, and C may then be assumed to have had similar treatment. Therefore, alloys M, K, O, and spherical must have had some fundamental processing differences from N, J, and C and amalgams made with them will be compared to amalgams made with the known partially processed alloys. The properties of amalgams made with alloy M are very similar to those of amalgams made with alloy D, the properties of amalgams made with alloy K are very similar to those of amalgams made with alloy B, and the properties of amalgams made with alloy O and the spherical alloy are similar to those of amalgams made with alloy L. Therefore, it might be assumed that alloy M was manufactured by just cutting the filings from an unannealed ingot and not annealing the filings, alloy K was manufactured by cutting the filings from an unannealed ingot and annealing the filings, and alloy O was manufactured by cutting the filings from a heat-treated ingot and not annealing the filings. These commercial alloys mentioned might have been carried through a complete processing cycle but some of the annealing or homogenizing steps might not have been sufficient or some sort of surface film, which is not desired, might have formed on the particles. All of these things would have affected the reaction rates. It is seen from the results that the incomplete processing affects the reaction more than the surface area of

the particles.

Error Analysis

In this research the reaction rate of the dental amalgam was based on the growth of the Ag_2Hg_3 phase. This growth was measured by the increase of intensity with time of the major peak, $2\theta = 38.0°$ (Cu Kα radiation) of the Ag_2Hg_3 phase. The second largest peak of the Ag_3Sn phase occurred at $2\theta = 37.6°$ (Cu Kα radiation) and the closeness of these two peaks will affect both their intensities making them larger than they should be. At the beginning of the reaction, the intensity of the 37.6° peak and the 38.0° peak is about the same. But, thereafter, with increasing time, the intensity of the 38.0° peak becomes much larger and, of course, the intensity of the 37.6° peak becomes smaller and the error becomes less.

Another source of error is the difference in the mass absorption coefficient of the elements and phases in question. It is shown that only a small amount of mercury is reacted during trituration. In fact, the same amount of mercury, regardless of the amount present, reacts for a given alloy. Therefore, for an amalgam with a large mercury content, much unreacted mercury is present in the sample after trituration. For Cu Kα radiation mercury has a mass absorption coefficient of 2,950 cm^{-1}, silver 2,285 cm^{-1}, tin 1,880 cm^{-1}, and Ag_2Hg_3 2,750 cm^{-1}. In amalgams where there would be an appreciable amount of unreacted mercury present, the intensity obtained at Ag_2Hg_3 peak would be lower than it should be.

$\text{Log} \frac{I\infty}{I\infty - It}$ versus time was plotted on log-log paper, and the

data points were to fall on a straight line. In most cases the first intensities obtained and plotted were not on the line because of the effects mentioned above. The two effects have a positive and negative effect on the intensities. Most of the first intensities that were not on the line were on the upper side of the straight line because of the closeness of the peaks, but some, in amalgams of high mercury content, were on the lower side of the straight line because of the mercury absorption of the x-rays. For first intensities that fell on the straight line, it could be assumed that the two sources of error were equal.

The error due to the closeness of the peaks decreases greatly after the first readings because the ratio of the peaks becomes very large quickly, and the error due to the mercury absorption also decreases quickly as the unreacted mercury reacts and disappears. All data points obtained after the first or second reading (usually after ten minutes of reaction) fell on a straight line, and from these lines the b values, n values, half-lives, etc. were obtained. There is considered to be very little error involved.

Discussion of Data

The discussion of the results of these studies is first treated separately for the amalgams made from commercial alloys and the amalgams made from the experimental alloys. The comparison of all the amalgams made in this study was given earlier in the Results section.

b Values (Amount of Reaction Taking Place During Trituration)

Commercial Alloys. The amalgams made with alloy M had the largest b value or the most reaction during trituration. This was true for all

percentages of mercury used although amalgams made with alloy O did have about the same b value at 60 and 60% (before squeezing) mercury. Amalgams made with alloy J had the least reaction during trituration or lowest b value for all mercury percentages except the lowest, 20%. At this percent mercury, amalgams made with alloys N and O had the lowest b value. The b value decreased with increasing mercury percentages in all cases but decreased least in amalgams made with alloy O.

Experimental Alloys. Amalgams made with alloy D had the most reaction during trituration as its b value was largest for all percentages of mercury used. Amalgams made with alloy C had the smallest b value for all percentages of mercury used. The b values of amalgams made with alloy C had the least change with increasing mercury percentages.

The percent of the total reaction that took place during trituration was calculated for each alloy and percent mercury used. The b value was equal to log $I_\infty/(I_\infty - I_t)$ at the y-intercept and from this I_t was found, and then $I_t/I_\infty(100)$ was calculated and considered to be the percent of the total reaction that took place during trituration. These numbers and the b values are given in Table 3. The schematic plots of b values versus % mercury for amalgams made with all alloys are given in Figures 4 and 5.

By multiplying the percent reaction that took place during trituration by the percent mercury present in the amalgam, it was seen that only a certain amount of mercury would be reacted during trituration and no more regardless of the amount of mercury present before trituration. So, the percent mercury reacted during trituration remained constant with increasing mercury percentages for all amalgams except those made with alloy C.

Table 3. b Values and % Total Reaction Taking Place During Trituration of Amalgams of All Alloys with Various Amounts of Mercury

Amalgam	Alloy	b	% Reaction During Trituration
20% Mercury	Commercial		
	M	1.235	71.2
	K	.510	40.0
	O	.258	22.7
	N	.266	22.9
	J	.484	38.3
	Experimental		
	D	.923	60.0
	B	.500	39.5
	L	.339	28.9
	A	.519	40.4
	C	.115	10.9
	Spherical	.575	43.8
30% Mercury	Commercial		
	M	.415	33.9
	K	.330	28.4
	O	.173	15.9
	N	.116	10.9
	J	.111	10.5
	Experimental		
	D	.392	32.4
	B	.260	23.1
	L	.183	16.7
	A	.120	11.3
	C	.104	9.9
	Spherical	.369	30.8
40% Mercury	Commercial		
	M	.318	27.2
	K	.199	18.2
	O	.168	15.7
	N	.088	8.3
	J	.078	7.5

Table 3. b Values and % Total Reaction Taking Place During Trituration of Amalgams of All Alloys with Various Amounts of Mercury (Concluded)

Amalgam	Alloy	b	% Reaction During Trituration
40% Mercury	Experimental		
	D	.369	30.8
	B	.196	17.8
	L	.138	12.9
	A	.111	10.5
	C	.052	5.1
	Spherical	.260	22.9
50% Mercury	Commercial		
	M	.172	15.8
	K	.171	15.7
	O	.167	15.5
	N	.083	7.9
	J	.074	7.1
	Experimental		
	D	.208	18.7
	B	.196	17.8
	L	.137	12.9
	A	.089	8.4
	C	.044	4.3
	Spherical	.127	11.9
60% Mercury	Commercial		
	M	.157	14.6
	K	.138	12.9
	O	.162	14.9
	N	.074	7.1
	J	.051	5.0
	Experimental		
	D	.196	17.8
	B	.164	15.1
	L	.102	9.7
	A	.082	7.8
	C	.041	4.1
	Spherical	.124	11.7
60% Mercury (Before Squeezing)	Commercial		
	M	.161	14.9
	K	.141	13.1
	O	.167	15.5
	N	.077	7.4
	J	.053	5.1

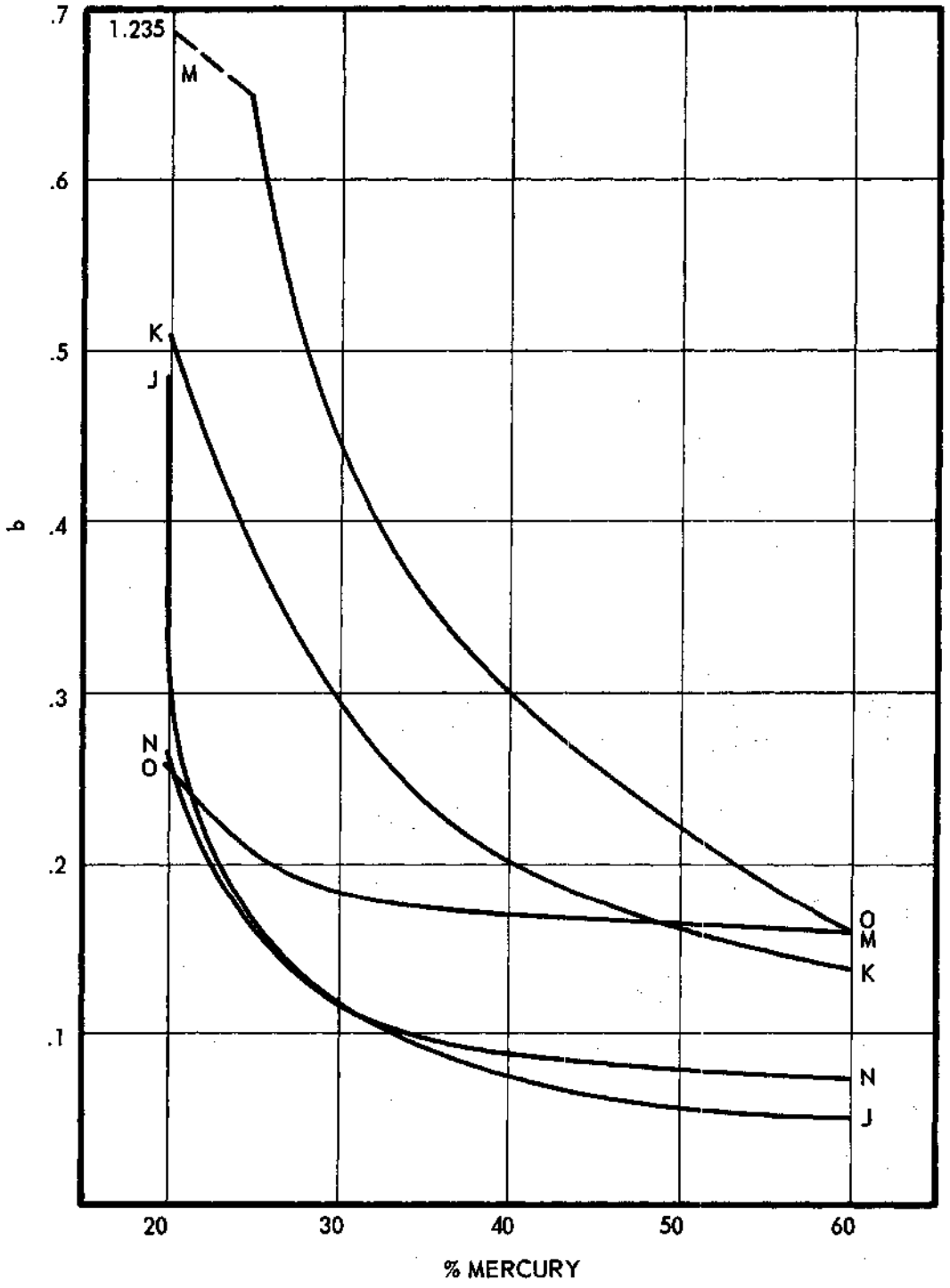

Figure 4. b versus % Mercury for Amalgams Made with Commercial Alloys.

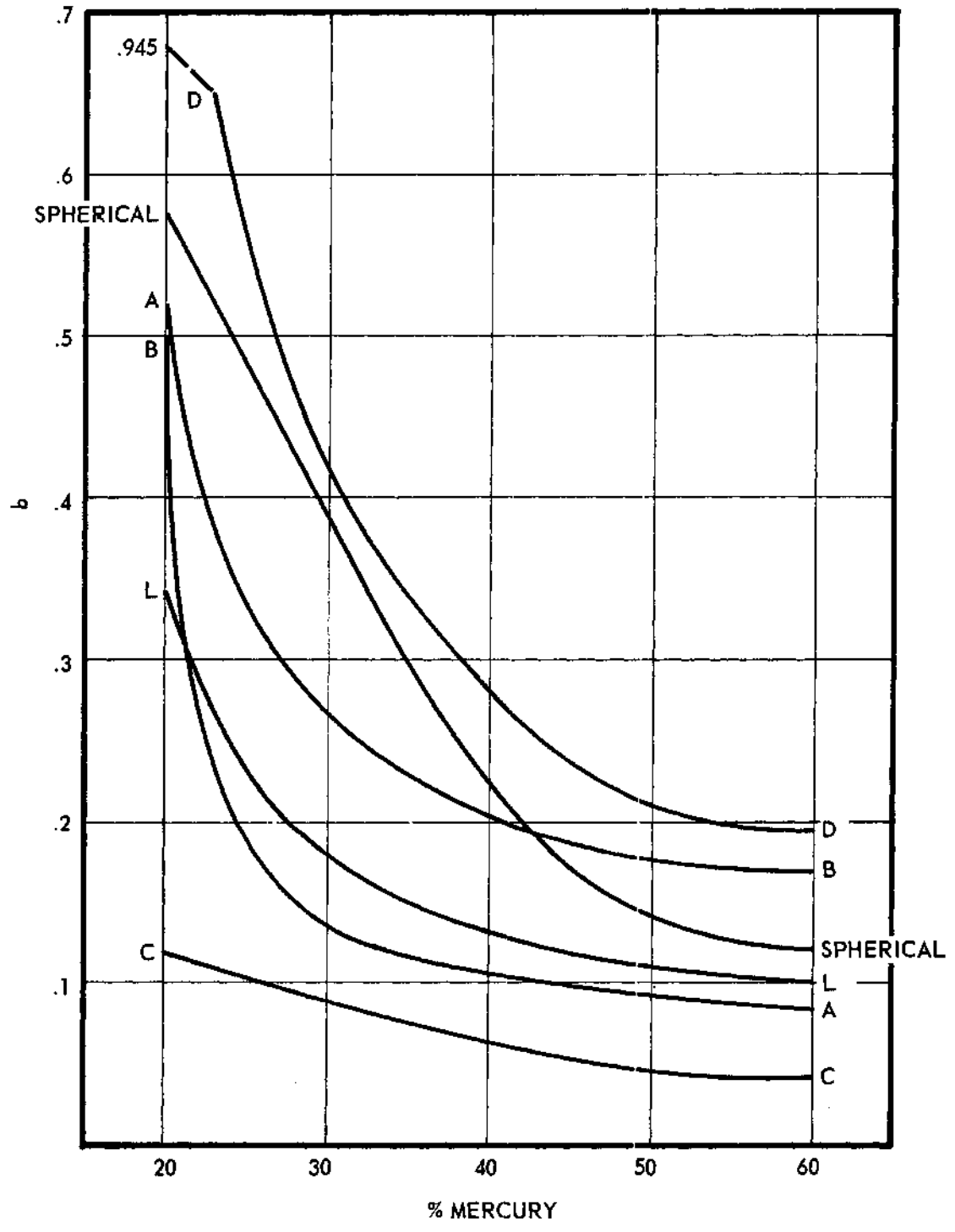

Figure 5. b versus % Mercury for Amalgams Made with Experimental Alloys.

Commercial Alloys. The largest amount of mercury reacted during trituration was found in amalgams made with alloy M. The least reacted was found in amalgams made with alloy J.

Experimental Alloys. The largest amount of mercury reacted during trituration was found in amalgams made with alloy D. The least reacted was found in amalgams made with alloy C.

These values are given in Table 4.

n Values (Reaction Rate After Trituration)

Commercial Alloys. Amalgams made with alloy J had the greatest slope or n value for all mercury percentages except the two lowest, 20 and 30%. Amalgams made with alloy N had the largest n values at 20 and 30% mercury. Amalgams made with alloy M had the lowest n values or reaction rate after trituration at 20, 40, and 60% mercury. Amalgams made with alloy O had the lowest n values at 30 and 50% mercury. Amalgams made with alloys N, K, and O had different n values, but these values did not change significantly with percent mercury.

Experimental Alloys. Amalgams made with alloy C had the largest n values for all mercury percentages. In a couple of cases, amalgams made with alloy A had the same n values as did the C alloy amalgams. Amalgams made with alloy D had the lowest n values at 20, 30, and 40% mercury. Amalgams made with alloy B had the lowest n values at 50 and 60% mercury. Amalgams made with alloy B had rather constant n values at all percentages mercury used.

These values are given in Table 5.

Half-Lives

Commercial Alloys. Amalgams made with alloy N had the longest

Table 4. Average % Mercury Reacted with All Alloys During Trituration Regardless of the Amount Mercury Present

Commercial Alloys	Average % Hg Reacted During Trituration	Experimental Alloys	Average % Hg Reacted During Trituration
M	10.0	D	11.0
K	8.0	B	8.0
O	7.0	L	5.8
N	4.0	A	4.5
J	3.5	C	2.3
		Spherical	8.0

Table 5. n Values of Amalgams of All Alloys with Various Amounts of Mercury

Amalgam	Commercial Alloys	n	Experimental Alloys	n
20% Mercury	M	.244	D	.336
	K	.438	B	.446
	O	.493	L	.695
	N	.513	A	.415
	J	.383	C	.759
			Spherical	.524
30% Mercury	M	.509	D	.508
	K	.477	B	.531
	O	.461	L	.785
	N	.600	A	.720
	J	.570	C	.665
			Spherical	.664
40% Mercury	M	.391	D	.454
	K	.473	B	.484
	O	.461	L	.790
	N	.565	A	.664
	J	.672	C	.808
			Spherical	.594
50% Mercury	M	.441	D	.594
	K	.460	B	.461
	O	.415	L	.570
	N	.526	A	.656
	J	.578	C	.781
			Spherical	.719
60% Mercury	M	.428	D	.531
	K	.507	B	.453
	O	.438	L	.531
	N	.500	A	.719
	J	.656	C	.711
			Spherical	.546
60% Mercury (Before Squeezing)	M	.469		
	K	.508		
	O	.406		
	N	.531		
	J	.640		

half-lives at all percentages of mercury used. Amalgams made with alloy M had the shortest half-lives at 20, 30, and 40% mercury. Amalgams made with alloy K had the shortest half-lives at 50 and 60% mercury.

Experimental Alloys. Amalgams made with alloy C had the longest half-lives and amalgams made with alloy D had the shortest half-lives for all percentages of mercury used.

These values are given in Table 6 and the schematic plots of the half-life of amalgams made with all the alloys versus mercury percentage are given in Figures 6 and 7.

Total Reaction Time

The total reaction time or time when the intensity changed no more was found for the amalgams made with each alloy. With higher percentages of mercury, extrapolation and estimation were used to get the total reaction time.

Commercial Alloys. Amalgams made with alloy D had the longest total reaction time at 20 and 30% mercury. Amalgams made with alloy N had the longest total reaction time at 40, 50, and 60% mercury. Amalgams made with alloy M had the shortest total reaction time at all mercury percentages except the largest, 60%. At 60% mercury, the amalgam made with alloy K had the shortest total reaction time.

Experimental Alloys. Amalgams made with alloy A had the longest total reaction time at 20% mercury, amalgams made with alloy C had the longest total reaction time at 30% mercury, and amalgams made with alloy B had the longest total reaction time at 40, 50, and 60% mercury. Amalgams made with alloy L had the shortest total reaction time at 20, 30, and 40% mercury and amalgams made with alloy D had the shortest total reaction

Table 6. Half-Lives of Amalgams of All Alloys with Various Amounts of Mercury

Amalgam	Commercial Alloys	Minutes ($t_{1/2}$)	Experimental Alloys	Minutes ($t_{1/2}$)
20% Mercury	M	0.1	D	0.04
	K	2.0	B	2.0
	O	7.4	L	2.8
	N	6.4	A	2.0
	J	2.5	C	11.0
			Spherical	1.4
30% Mercury	M	2.7	D	3.1
	K	4.8	B	6.3
	O	20.0	L	5.5
	N	20.0	A	11.4
	J	25.0	C	17.4
			Spherical	2.6
40% Mercury	M	7.4	D	4.0
	K	14.0	B	13.7
	O	21.5	L	7.7
	N	38.5	A	16.0
	J	25.9	C	24.6
			Spherical	5.2
50% Mercury	M	23.7	D	7.6
	K	21.0	B	15.5
	O	29.0	L	17.0
	N	56.0	A	23.0
	J	48.0	C	34.0
			Spherical	10.6
60% Mercury	M	32.5	D	10.8
	K	24.0	B	24.0
	O	25.0	L	37.0
	N	88.0	A	19.5
	J	56.0	C	53.0
			Spherical	23.4
60% Mercury (Before Squeezing)	M	24.0		
	K	23.0		
	O	33.0		
	N	62.0		
	J	56.0		

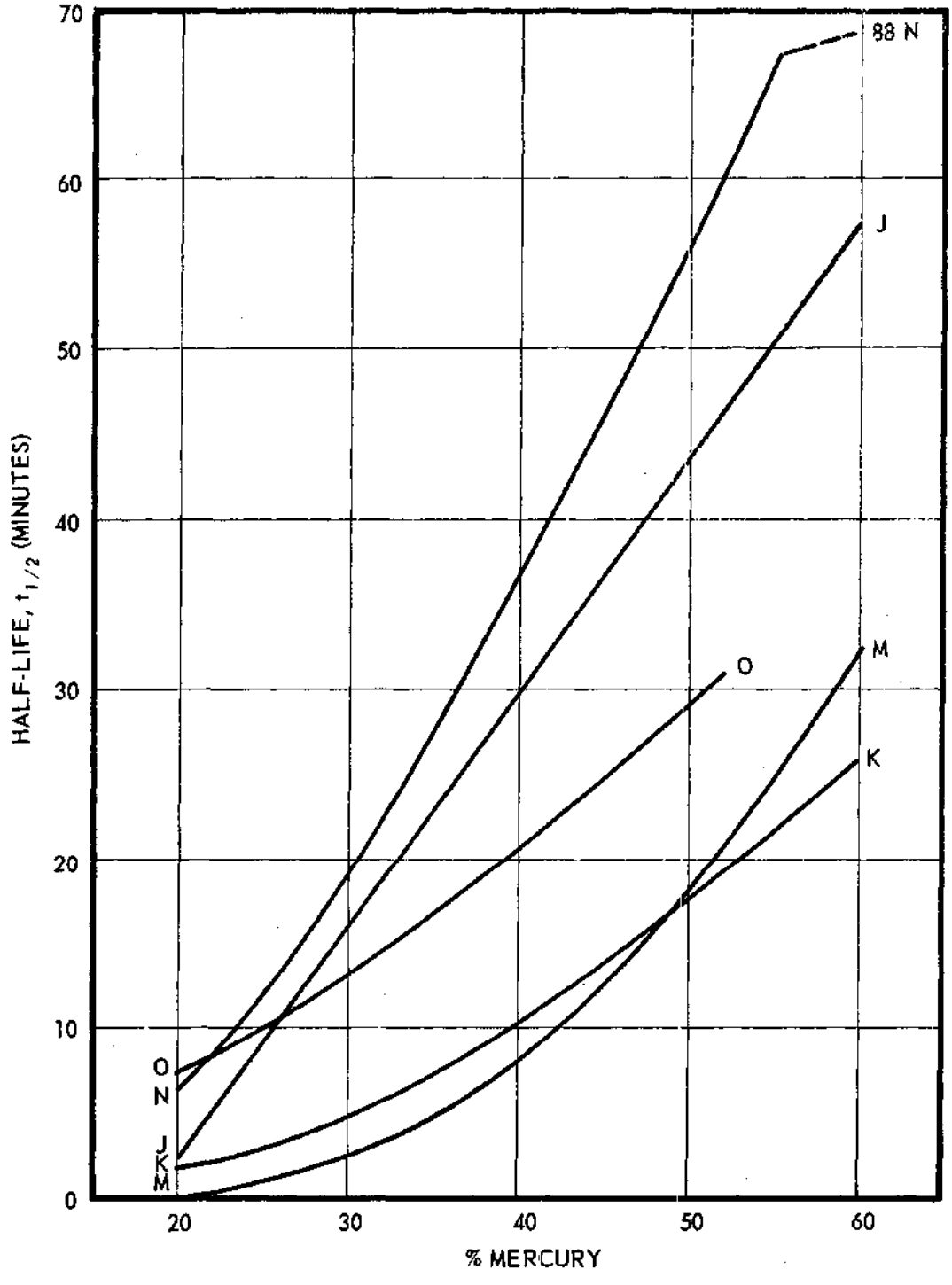

Figure 6. Half-Life versus % Mercury for Amalgams Made with Commercial Alloys.

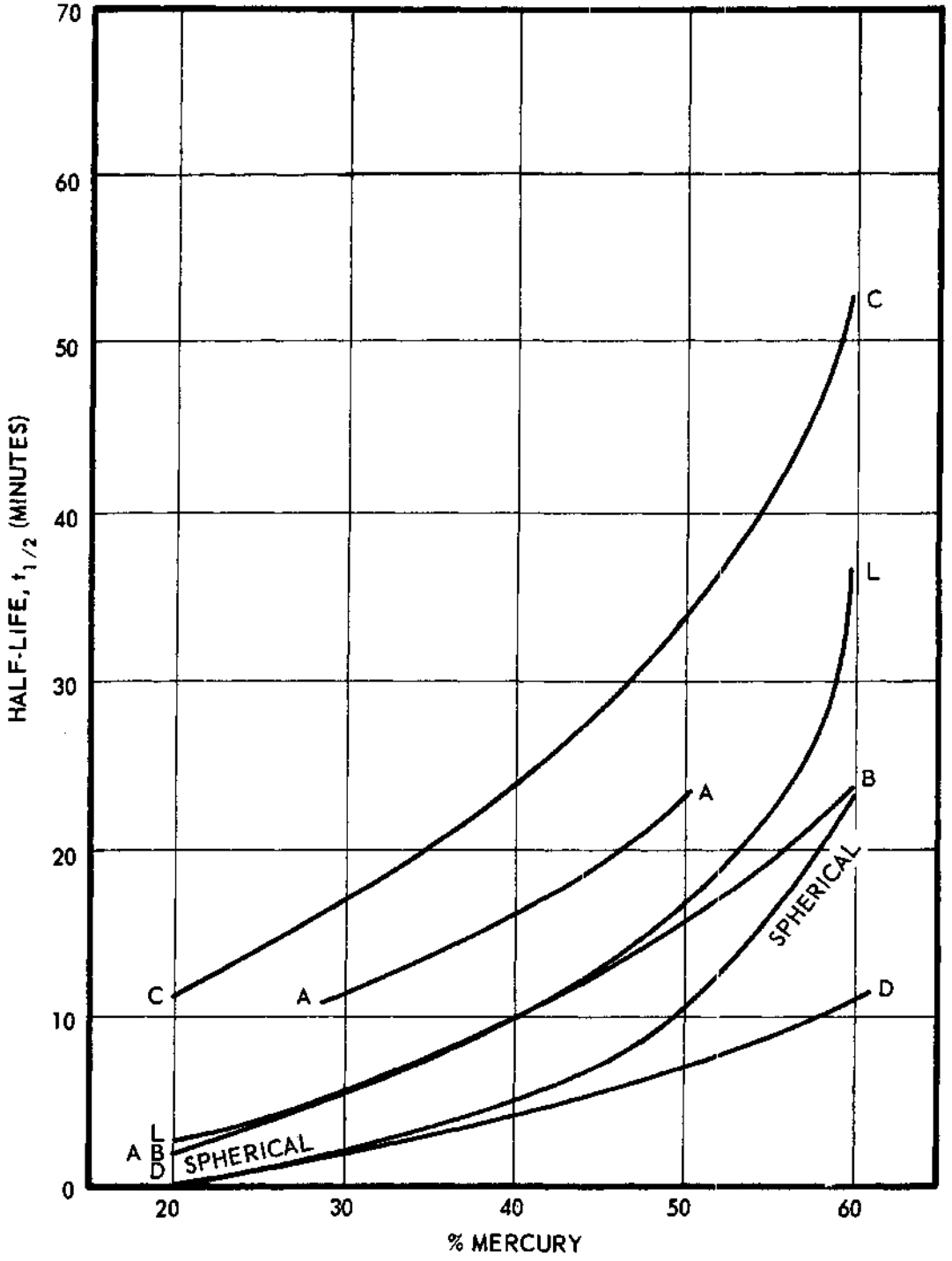

Figure 7. Half-Life versus % Mercury for Amalgams Made with Experimental Alloys.

time at 50 and 60% mercury.

These values are given in Table 7 and the schematic plots of total reaction time of the amalgams of each alloy versus mercury percentages are found in Figures 8 and 9.

Trituration Time

The average trituration time needed for each alloy and mercury is found in Table 8. Trituration time did not depend on the amount of mercury present.

Particle Size and Surface Area

The particle size and surface area of each alloy powder is given in Table 9.

Many dentists make the amalgam with about 60% mercury and then squeeze the plastic mass with a cotton squeeze cloth to express (remove) free mercury. This more hardened mass of less than 60% mercury is then condensed into the cavity and allowed to fully harden. Amalgams made from mixtures where some of the mercury was squeezed out showed reaction rate properties (b, n, etc.) like an amalgam of less than 60% mercury composition of the same alloy. It is, therefore, suggested and substantiated by the data in this work that the lower percent mercury amalgam will achieve the same purpose as higher percentages plus squeezing. Squeezing only introduces another job for the dentist as well as wasting a certain amount of mercury. The Eames Technique, from the reaction rate viewpoint, appears to be an ideal solution.

The x-ray diffraction observation of the amalgam samples during hardening showed the Ag_3Sn characteristic lines with larger than usual d-spacings which would be caused by the mercury in solution in the Ag_3Sn,

Table 7. Total Reaction Time of Amalgams of All Alloys with Various Amounts of Mercury

Amalgam	Commercial Alloys	Minutes t_∞	Experimental Alloys	Minutes t_∞
20% Mercury	M	87	D	40
	K	95	B	53
	O	240	L	25
	N	150	A	75
	J	180	C	56
			Spherical	47
30% Mercury	M	50	D	55
	K	120	B	120
	O	310	L	38
	N	160	A	90
	J	240	C	152
			Spherical	47
40% Mercury	M	190	D	88
	K	230	B	266
	O	340	L	70
	N	380	A	114
	J	170	C	171
			Spherical	110
50% Mercury	M	380	D	153
	K	320	B	400
	O	600	L	225
	N	650	A	260
	J	420	C	275
			Spherical	140
60% Mercury	M	600	D	360
	K	350	B	850
	O	600	L	750
	N	1000	A	270
	J	420	C	600
			Spherical	650
60% Mercury (Before Squeezing)	M	400		
	K	330		
	O	600		
	N	650		
	J	420		

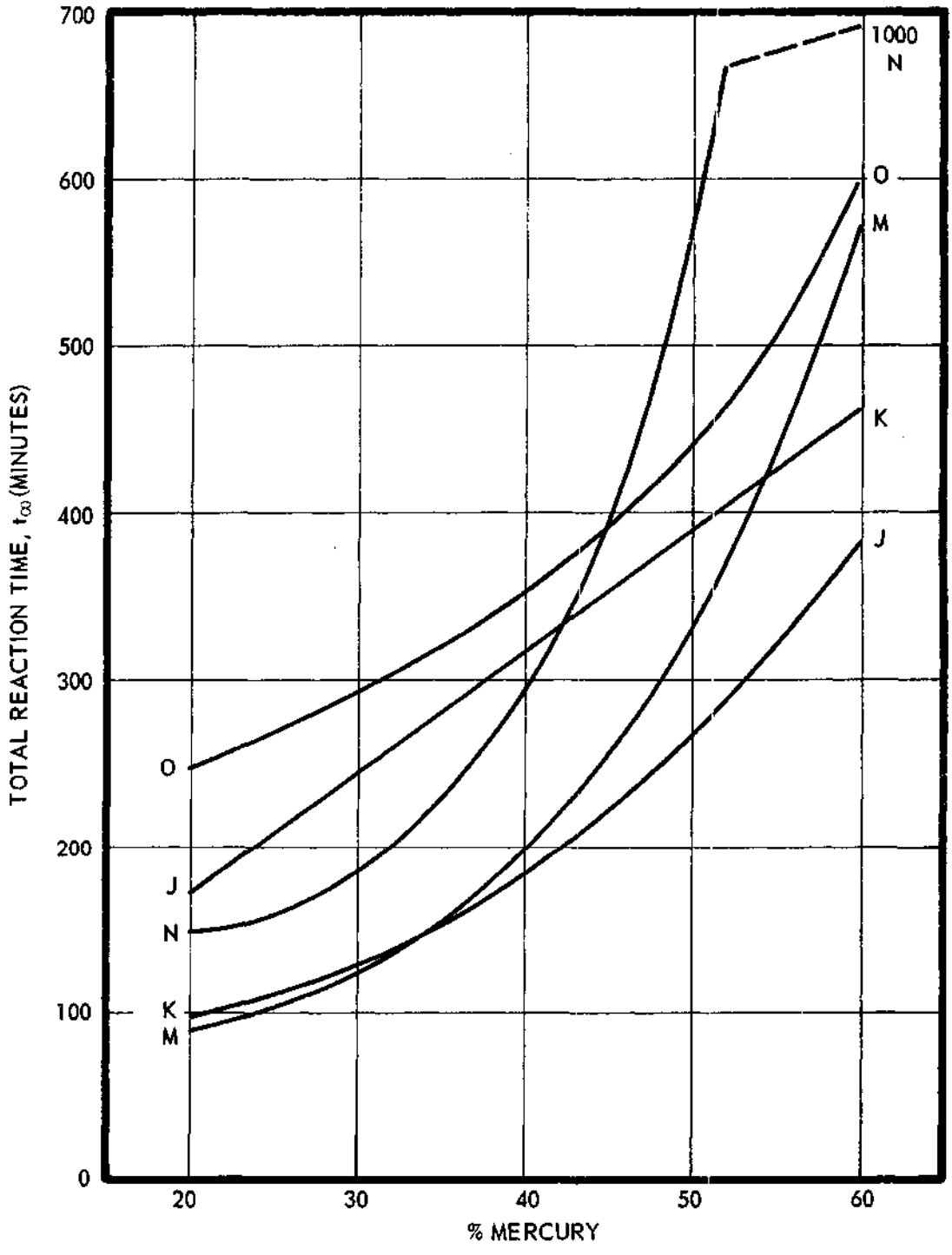

Figure 8. Total Reaction Time versus % Mercury for Amalgams Made with Commercial Alloys.

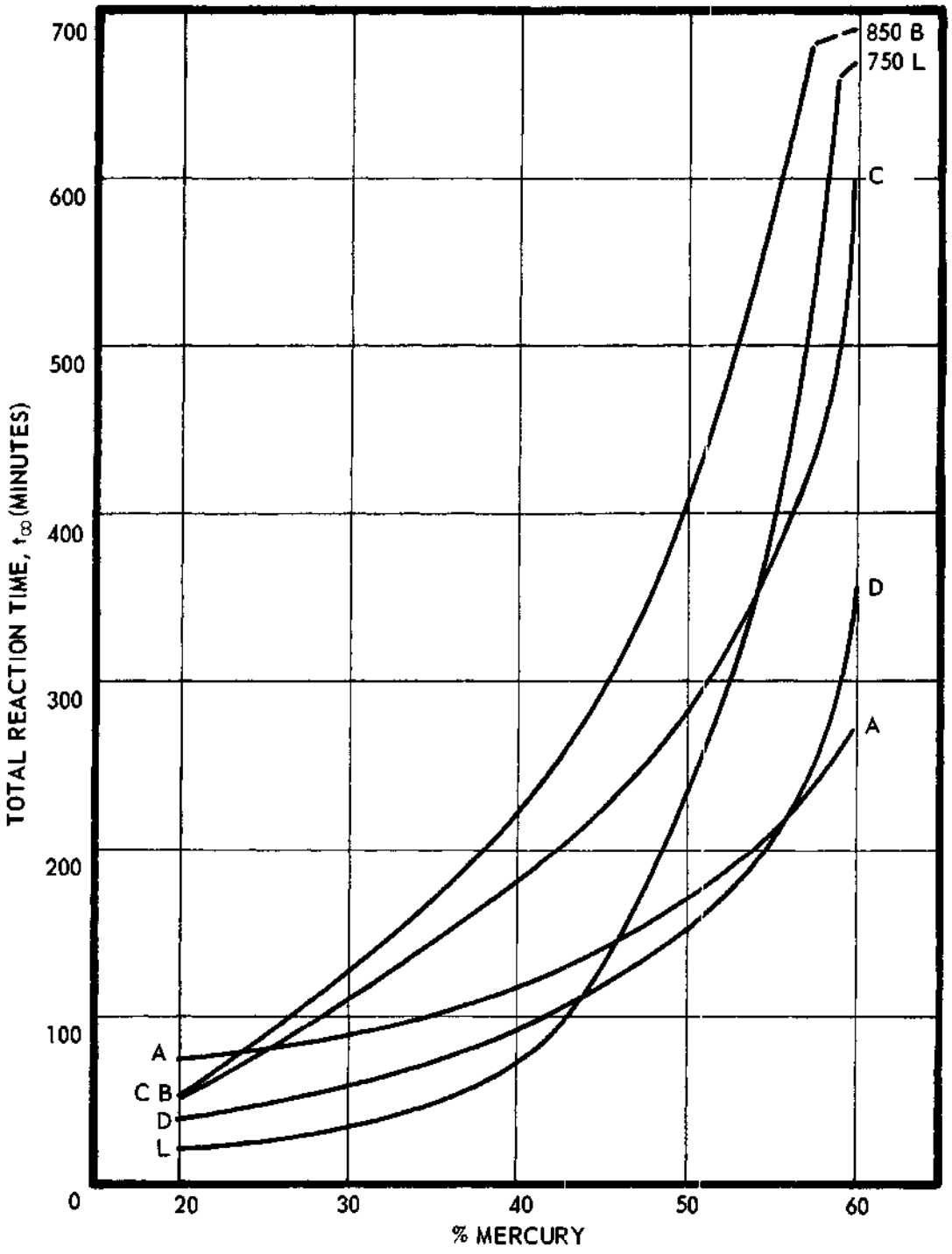

Figure 9. Total Reaction Time versus % Mercury for Amalgams Made with Experimental Alloys.

Table 8. Average Trituration Times for Alloys with Any Amount of Mercury (Time to Develop a Plastic Workable Mass with No Excess Mercury)

Alloy	Trituration Time-Average for All Mercury Percentages (Seconds)
Commercial	
M	60
K	40
O	52
N	48
J	60
Experimental	
D	37
B	39
L	35*
A	47
C	52
Spherical	65

*Very few samples

Table 9. Particle Size and Surface Area of All Alloy Powders

Alloy	Surface Area (m^2/g)	Mean Diameter (Microns)	Deviation (σ g)
Commercial			
M	.127	22	1.36
K	.108	28	1.41
O	.078	36	1.61
N	.131	25	1.44
J	.107	25	1.39
Experimental			
D	.099	26	1.35
B	.098	26	1.38
L	.069	30	1.35
A	.111	26	1.35
C	.095	26	1.60
Spherical	.060	22.5	1.47

Surface Area was obtained through the use of the Brunauer, Emmett, and Teller procedure (37).

Particle size was obtained in a Sharples Micromarograph using their standard procedure.

($Ag_3Sn(Hg)$). The characteristic lines and intensities of the γ, γ_1, and γ_2 phases as observed in this work are given in Table 10.

In a couple of cases a very broad and short peak was observed at about $2\theta = 34^\circ$ (Cu Kα radiation). The peak would quickly disappear and was found to be a characteristic peak of liquid mercury. This was not desired in this work as it meant some free mercury had been condensed out from the amalgam.

The two major peaks of the Sn_8Hg phase are 30.0 and 32.2° 2θ (Cu Kα radiation). The 32.2° 2θ peak should have the largest intensity (from actual observation or calculation), but results have been reported in the literature and were obtained in some of this work with highly compressed amalgams showing the 30.0° 2θ peak with the largest intensity. This phenomena could be due to preferred orientation since the 30.0° 2θ peak is from the basal plane of the Sn_8Hg hexagonal lattice. A pole figure study of this peak, indeed, confirmed the preferred orientation.

The intensity of the 37.6° 2θ peak of the $Ag_3Sn(Hg)$ solid solution phase was also shown to be larger than the intensity of the 39.6° 2θ peak in cases of highly compressed amalgams. This was also shown to be due to preferred orientation.

From this work, it is concluded that the reaction of mercury with the silver-tin alloy is merely a chemical-type reaction which can be written:

$$Hg + \gamma \rightarrow \gamma_1 + \gamma_2 + \text{unreacted } \gamma \qquad \text{or}$$

$$Hg + Ag_3Sn \rightarrow Ag_2Hg_3 + Sn_8Hg + Ag_3Sn(Hg)$$

Table 10. Characteristic X-Ray Diffraction Patterns of Phases That Make Up Dental Amalgam

Ag_3Sn Phase				Ag_2Hg_3 Phase				Sn_8Hg Phase (18% Hg)			
2θ	d	I/I_o	hkl	2θ	d	I/I_o	hkl	2θ	d	I/I_o	hkl
34.6	2.59	25	110,020	25.1	3.55	3	220	30.0	2.98	36	001
37.6	2.39	50	002	30.9	2.89	11	222	32.2	2.78	100	100
39.6	2.27	100	111,021	33.5	2.67	15	321	44.4	2.04	76	101
52.0	1.76	15	112,022	38.0	2.37	100	330,411	57.2	1.61	16	110
61.9	1.50	10	200,130	40.2	2.24	10	420	61.8	1.50	4	002
69.2	1.36	20	113,023	42.6	2.12	10	332	66.0	1.41	18	111
74.7	1.27	16	202	44.2	2.04	5	422	67.5	1.39	8	200
76.0	1.25	12	221	46.1	1.97	14	510,431	71.5	1.32	16	102
				49.8	1.83	8	521				
				55.2	1.66	11	600,442				
				59.8	1.54	5	541				
				63.0	1.47	8	631				
				64.4	1.45	10	444				
				65.7	1.42	11	710,543				
				68.7	1.37	22	721,552				
				74.4	1.27	10	651,732				
				77.2	1.24	15	811,741				

It is also concluded that both the γ_1 and γ_2 phases start forming at the same time but since much less γ_2 phase is formed, its characteristic lines are sometimes not seen at the very beginning of the reaction.

Using material balance techniques, the amounts of each phase that would be expected to form from a given amount of mercury and alloy and a sample calculation are given in Table 11.

A quantitative analysis procedure was attempted on certain powdered amalgam samples to see how it might be applied to work of this sort. Quantitative analysis by diffraction is based on the fact that the intensity of the diffraction pattern of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture. The relation between intensity and concentration is not generally linear, since the diffracted intensity depends markedly on the absorption coefficient of the mixture and this itself varies with the concentration. The quantitative scheme cannot be used with inexactly defined crystal sizes. This presents a problem in the hardening or amalgamation reaction where new phases are growing. Some experimental results on powdered reacted samples are given in Appendix B.

Table 12 and Table 13 give a summary of all the results obtained in this work for all alloys and all amounts of mercury used.

Table 11. % of Certain Phases Expected from the Reaction of Mercury with the Silver-Tin Alloy

% Hg	+	% Ag_3Sn	→	% Ag_2Hg_3	+	% Sn_8Hg	+	% Ag_3Sn
20		80		26.0		3.3		70.7
30		70		39.0		5.0		56.0
40		60		52.0		6.6		41.4
50		50		65.0		8.2		26.8
60		40		78.1		9.8		12.1
69		31		86.8		13.2		0

Sample calculations for 20% Hg amalgam assume 10,000 weight units.

Material	MW	Wt %	Moles
Hg	200.61	20	10
Ag_3Sn	442.34	80	18.2
Ag_2Hg_3	817.59	A	X
Sn_8Hg	1150.21	B	Y
Ag_3Sn	442.34	C	Z

$$2X + 3Z = 54.6 \quad \text{Ag balance}$$
$$8Y + Z = 18.2 \quad \text{Sn balance}$$
$$3X + Y = 10 \quad \text{Hg balance}$$

Solve the three equations and get X, Y and Z.

$$\frac{817.59\ X}{10{,}000} = A = 26.0\%$$

$$\frac{1150.21\ Y}{10{,}000} = B = 3.3\%$$

$$\frac{442.34\ Z}{10{,}000} = C = 70.7\%$$

Table 12. Summary of All Results Obtained in the Observation of the Amalgamation Reaction (Commercial Alloys)

Comm. Alloy	% Hg	(Sec.) Trit. Time	b	% Reac. dur. Trit.	n	(Min.) $t_{1/2}$	(Min.) t_{∞}	1. I/I_o	*2. I/I_o	2. I/I_o
J	20	60	.484	38.3	.383	2.5	180	5	100	69
	30	60	.111	10.5	.570	25.0	240	6	100	34
	40	60	.078	7.5	.672	25.9	170	7	100	18
	50	60	.074	7.1	.578	48.0	420	14	100	9
	60	75	.051	5.0	.656	56.0	420	32	100	5
	60**	60	.053	5.1	.640	56.0	420	12	100	7
K	20	50	.510	40.0	.438	2.0	95	3	100	57
	30	40	.330	28.4	.477	4.8	120	5	100	40
	40	30	.199	18.2	.473	14.0	230	8	100	12
	50	35	.171	15.7	.460	21.0	320	12	100	6
	60	45	.138	12.9	.507	24.0	350	13	100	0
	60**	--	.141	13.1	.508	23.0	330	8	100	1
O	20	55	.258	22.7	.493	7.4	240	7	100	54
	30	45	.173	15.9	.461	20.0	310	9	100	35
	40	55	.168	15.7	.461	21.5	340	13	100	24
	50	45	.167	15.5	.415	29.0	600	15	100	5
	60	50	.162	14.9	.438	25.0	600	17	100	0
	60**	60	.167	15.5	.406	33.0	600	18	100	2
M	20	60	1.235	71.2	.244	0.1	87	4	100	68
	30	60	.415	33.9	.509	2.7	50	4	100	46
	40	60	.318	27.2	.391	7.4	190	4	100	27
	50	--	.172	15.8	.441	23.7	380	3	100	17
	60	60	.157	14.6	.428	32.5	600	10	100	4
	60**	60	.161	14.9	.469	24.0	400	9	100	7
N	20	50	.266	22.9	.513	6.4	150	4	100	46
	30	45	.116	10.9	.600	20.0	160	6	100	22
	40	45	.088	8.3	.565	38.5	380	8	100	12
	50	45	.083	7.9	.526	56.0	650	10	100	5
	60	60	.074	7.1	.500	88.0	1000	10	100	0
	60**	50	.077	7.4	.531	62.0	650	15	100	1

*Relative intensities of the major peaks of the three phases in dental amalgam.

1. $2\theta = 32.2°$ (Cu Kα radiation) Sn_8Hg phase
2. $2\theta = 38.0°$ Ag_2Hg_3 phase
3. $2\theta = 39.6°$ $Ag_3Sn(Hg)$ phase

**Before squeezing.

Table 13. Summary of All Results Obtained in the Observation of the Amalgamation Reaction (Experimental Alloys)

Exper. Alloy	% Hg	(Sec.) Trit. Time	b	% Reac. dur. Trit.	n	(Min.) t	(Min.) t	1. I/I_o	*2. I/I_o	3. I/I_o
L	20	--	.339	28.9	.695	2.8	25	9	100	63
	30	--	.183	16.7	.785	5.5	38	6	100	26
	40	45	.138	12.9	.790	7.7	70	5	100	7
	50	30	.137	12.9	.570	17.0	225	16	100	4
	60	--	.102	9.7	.531	37.0	750	16	100	2
	60**	30	.106	10.0	.617	21.0	250	24	100	0
A	20	50	.519	40.4	.415	2.0	75	6	100	94
	30	45	.120	11.3	.720	11.4	90	6	100	31
	40	50	.111	10.5	.664	16.0	114	7	100	16
	50	50	.089	8.4	.656	23.0	260	6	100	10
	60	45	.082	7.8	.719	19.5	270	14	100	1
B	20	45	.500	39.5	.446	2.1	53	5	100	67
	30	35	.260	23.1	.531	6.3	120	4	100	56
	40	35	.196	17.8	.484	13.7	266	7	100	24
	50	40	.196	17.8	.461	15.5	400	8	100	14
	60	40	.164	15.1	.453	24.0	850	13	100	5
C	20	50	.115	10.9	.759	11.0	56	6	100	83
	30	45	.104	9.9	.665	17.4	152	6	100	37
	40	50	.052	5.1	.808	24.6	171	6	100	21
	50	55	.044	4.3	.781	34.0	275	9	100	5
	60	60	.041	4.1	.711	53.0	600	7	100	0
D	20	40	.923	60.0	.336	.04	40	4	100	44
	30	35	.392	32.4	.508	3.1	55	5	100	30
	40	35	.369	30.8	.454	4.0	88	4	100	16
	50	40	.208	18.7	.594	7.6	153	8	100	8
	60	35	.196	17.8	.531	10.8	360	3	100	0
Spherical	20	65	.575	43.8	.524	1.4	47	5	100	77
	30	60	.369	30.8	.664	2.6	47	4	100	38
	40	65	.260	22.9	.594	5.2	110	2	100	16
	50	65	.127	11.9	.719	10.6	140	3	100	19
	60	65	.124	11.7	.546	23.4	650	7	100	8

*Relative intensities of the major peaks of the three phases in dental amalgam.

1. $2\theta = 32.2°$ (Cu Kα radiation) Sn_8Hg phase
2. $2\theta = 38.0°$ Ag_2Hg_3 phase
3. $2\theta = 39.6°$ $Ag_3Sn(Hg)$ phase

**Before squeezing.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

From this research work it was concluded that:

1. Surface area or particle size and the processing through which an alloy was carried affect the reaction rate, the processing being the more important variable.

2. Increased cold-work of the particles decreased the total time of reaction.

3. The percent of the total reaction that takes place during trituration varied from 4 to 71 depending on the amount of mercury and the alloy.

4. The percent mercury that would react during trituration regardless of the amount present varied from 2 to 11 depending on the type alloy.

5. The total time of reaction varied from 25 to 1,000 minutes depending on the amount of mercury and the alloy.

6. A "dry mix" technique with no condensation, such as the Eames Technique, produced a good amalgam from the reaction rate standpoint.

Recommendations for Further Research

It is recommended that a diffusion study of the mercury-silver-tin system be studied, as this may give a different viewpoint of the reaction rate.

It is recommended that a detailed study be made on ingots of the silver-tin alloy after casting and before and after heat treatment.

It is recommended that some physical property measurements be made with various alloys of incomplete processing to note the effect.

It is recommended that reaction rate studies be performed as was done in this work at a temperature of 37° C. (98.6° F.--body temperature) to ascertain the effects of the variables at this elevated temperature.

It is recommended that reaction rate studies be performed as was done in this work with the samples being under the influence of vibration or ultrasonic energy.

APPENDIX A

EXPERIMENTAL RESULTS

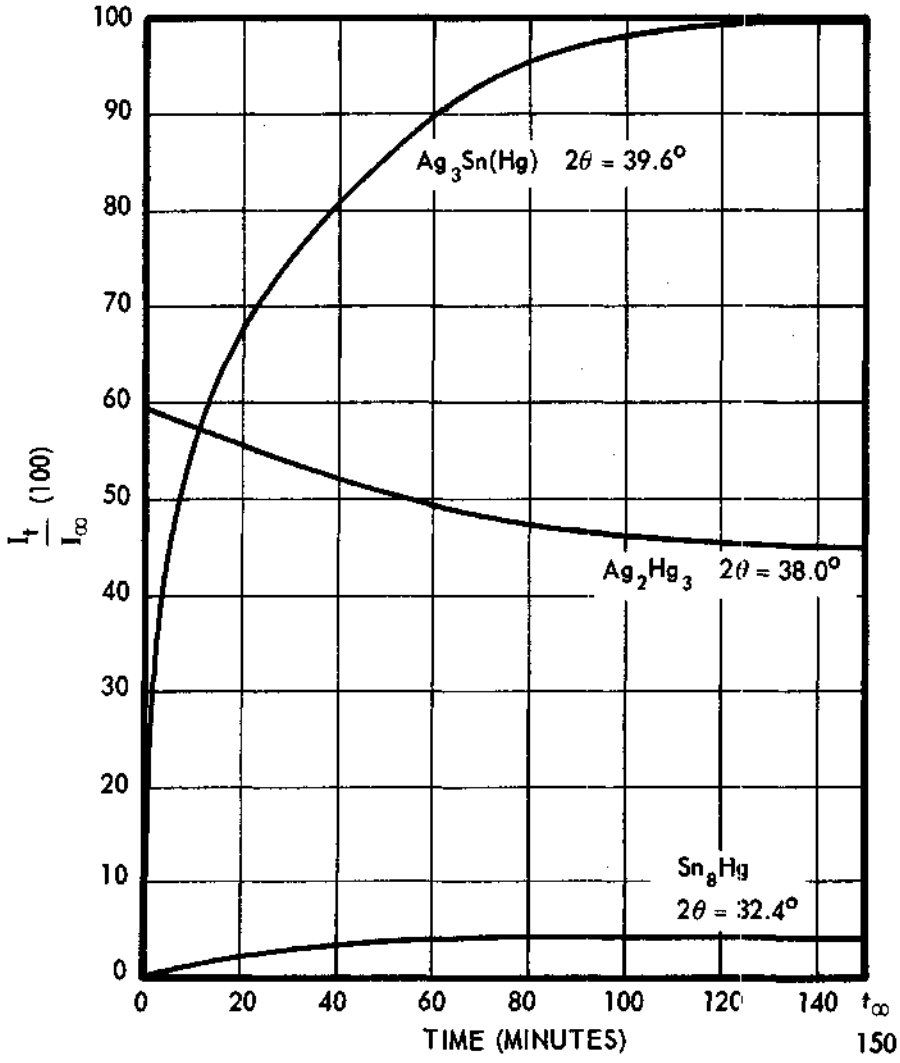

Figure A-1. Relative Intensities versus Time of the Major Peaks of the Phases of a 20% Mercury Amalgam Made with Alloy N.

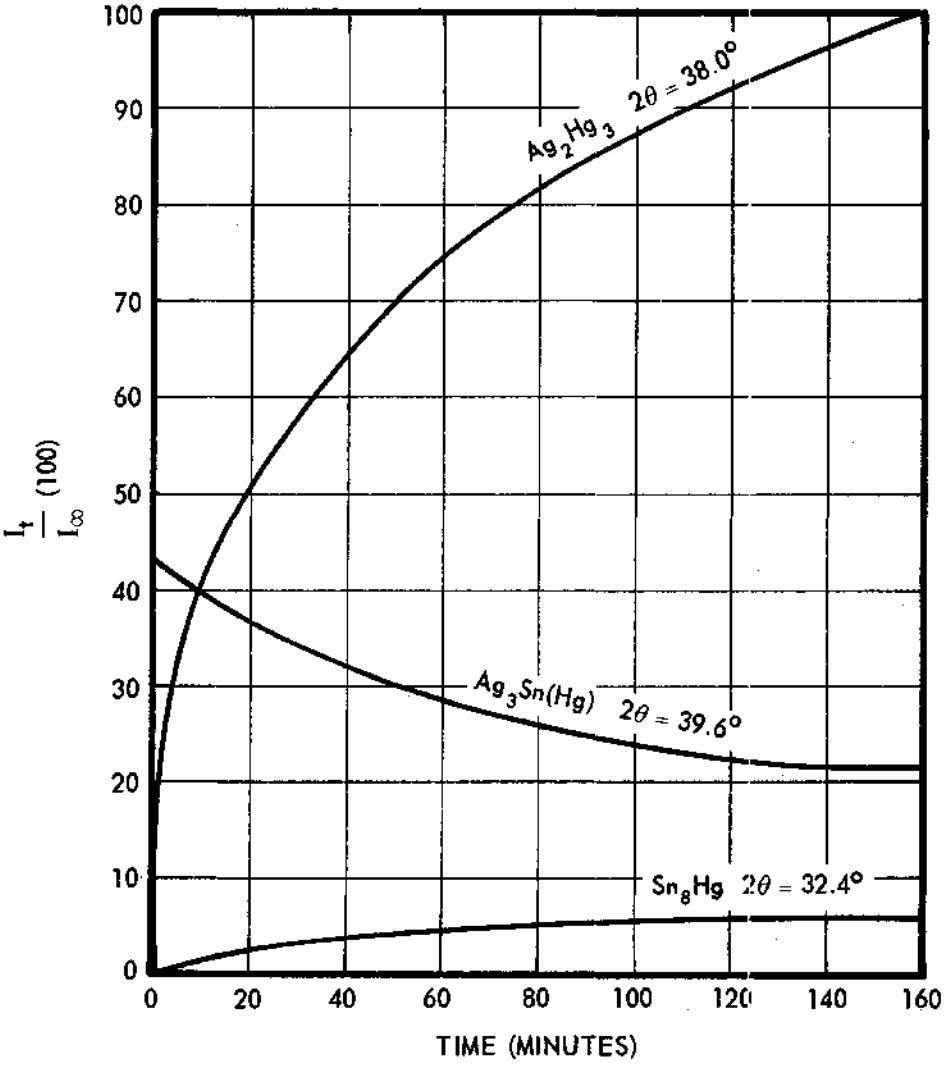

Figure A-2. Relative Intensities versus Time of the Major Peaks of the Phases of a 30% Mercury Amalgam Made with Alloy N.

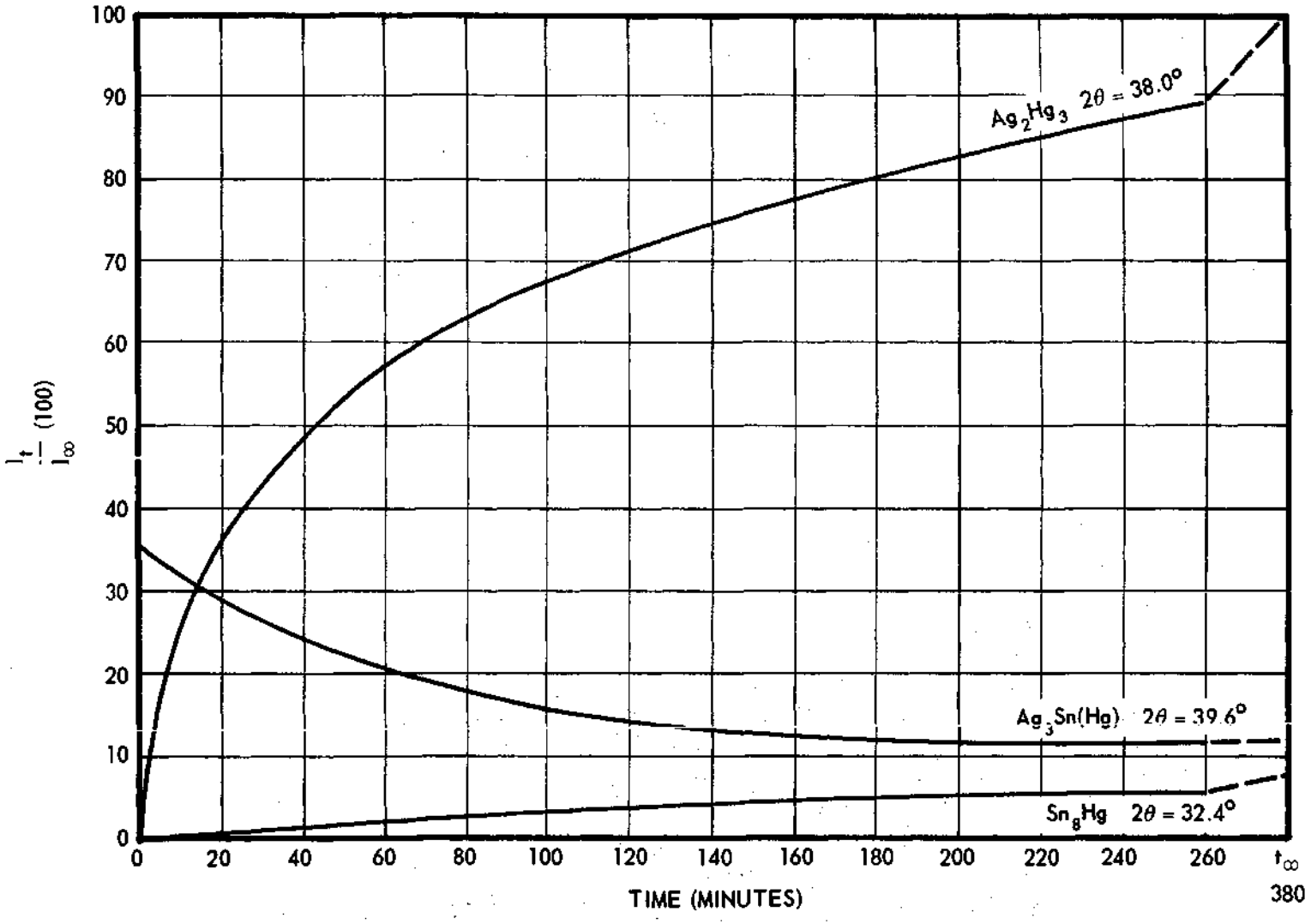

Figure A-3. Relative Intensities versus Time of the Major Peaks of the Phases of a 40% Mercury Amalgam Made with Alloy N.

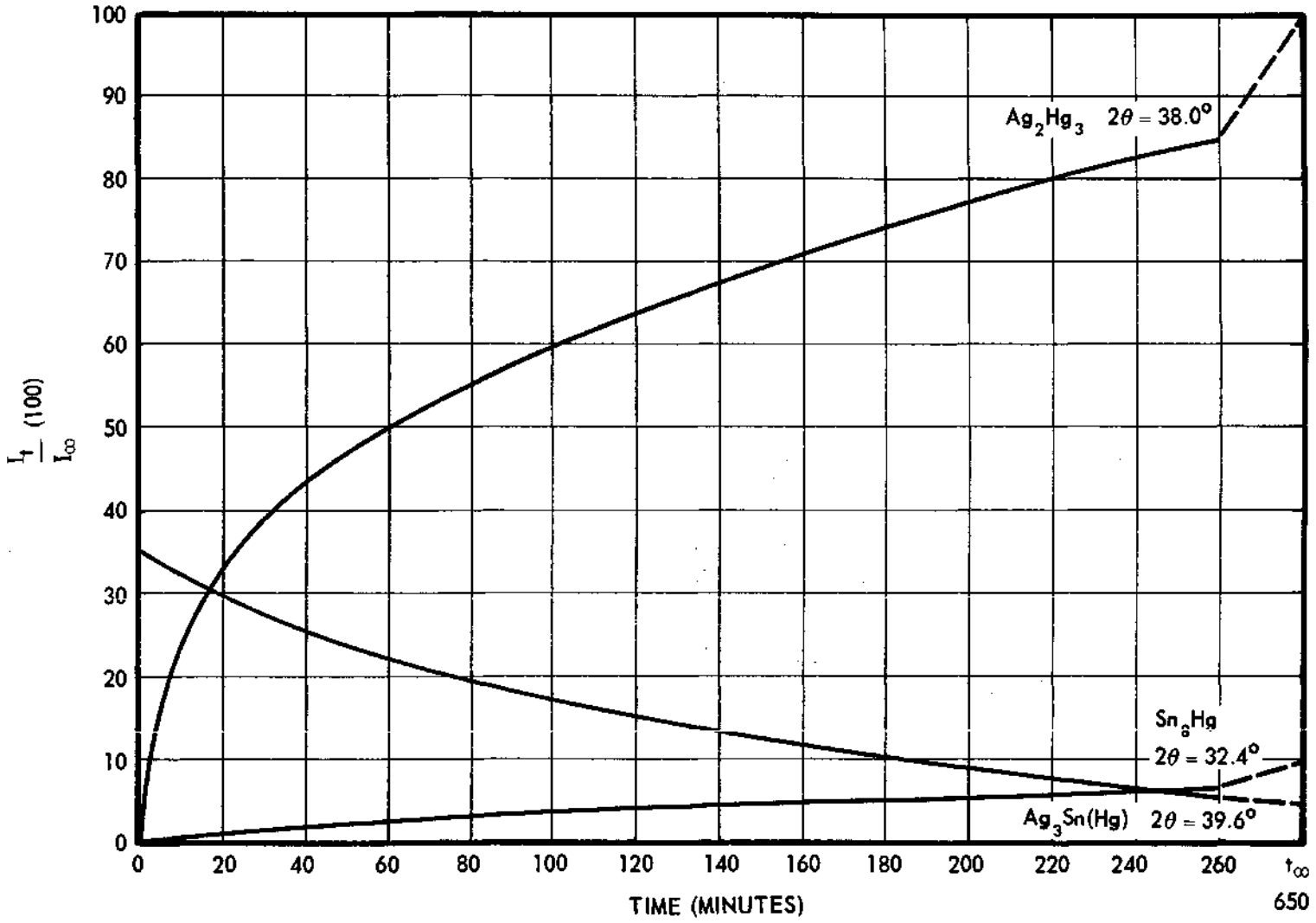

Figure A-4. Relative Intensities versus Time of the Major Peaks of the Phases of a 50% Mercury Amalgam Made with Alloy N.

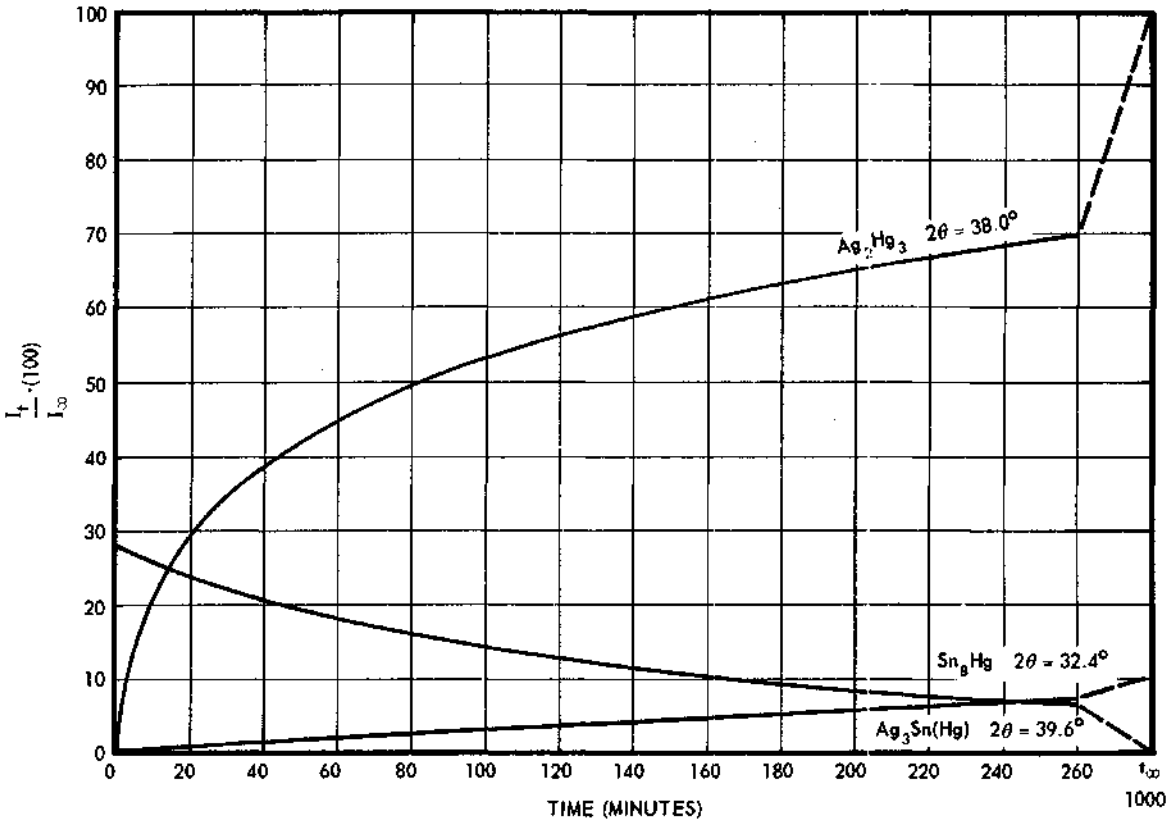

Figure A-5. Relative Intensities versus Time of the Major Peaks of the Phases of a 60% Mercury Amalgam Made with Alloy N.

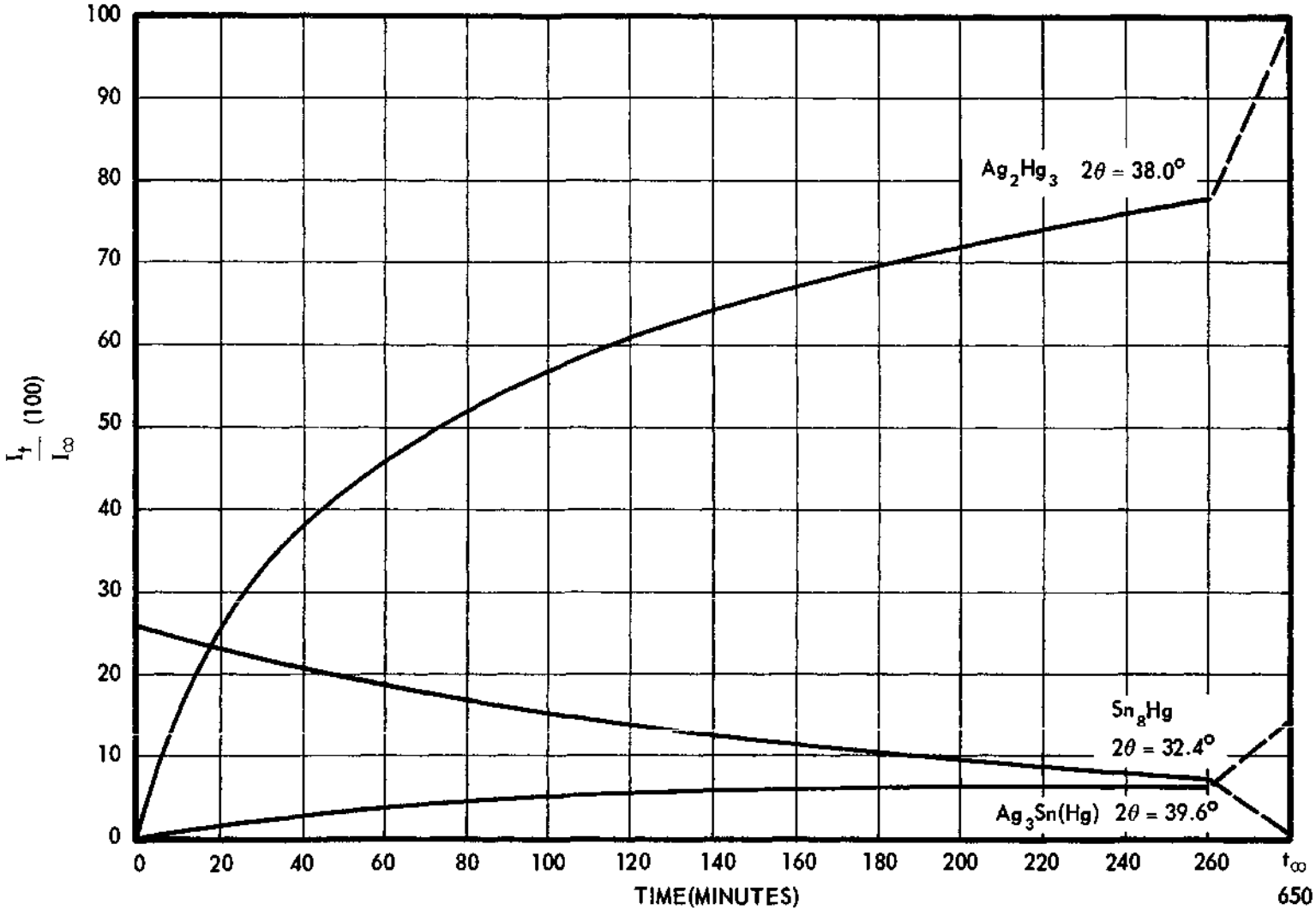

Figure A-6. Relative Intensities versus Time of the Major Peaks of the Phase of a 60% Mercury Amalgam (Before Squeezing) Made with Alloy N.

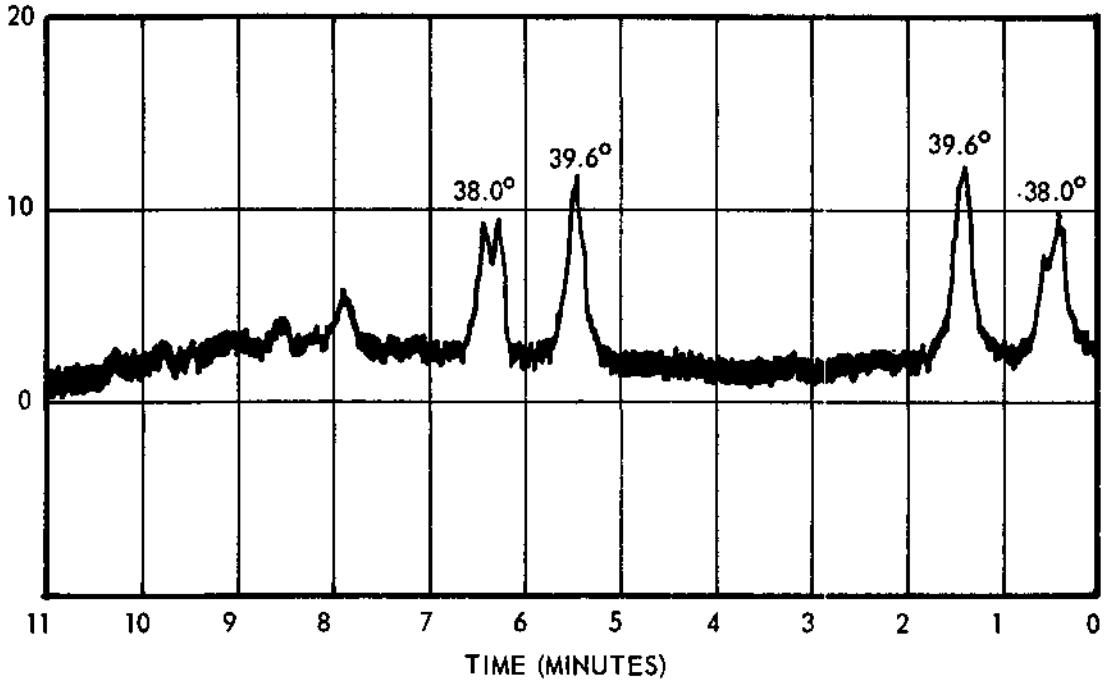

Figure A-7. Actual Diffraction Peaks of the Phases Formed in 60% Mercury Amalgams Made with Alloy C at a Given Time.

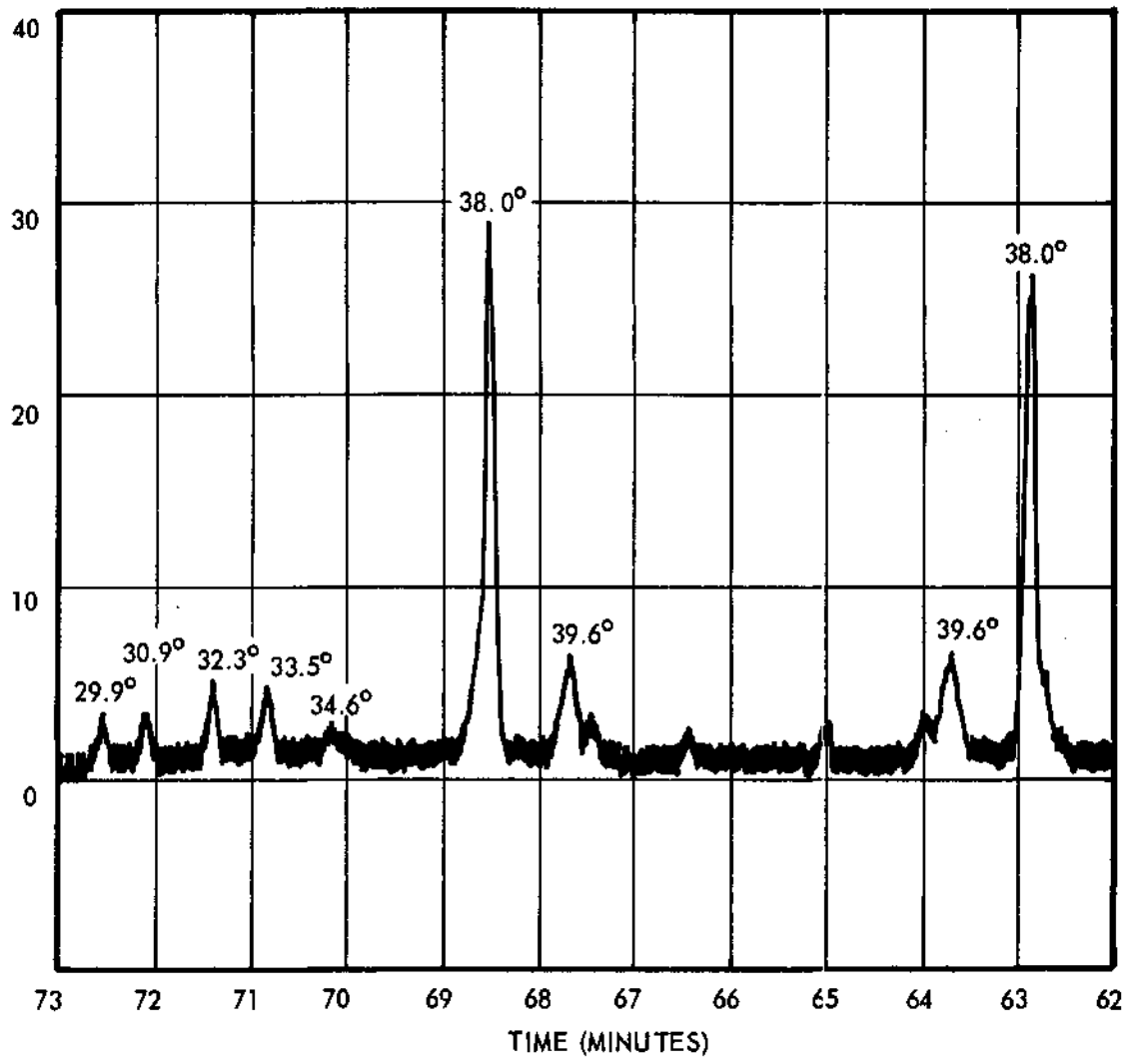

Figure A-8. Actual Diffraction Peaks of the Phases Formed in 60% Mercury Amalgams Made with Alloy C at a Given Time.

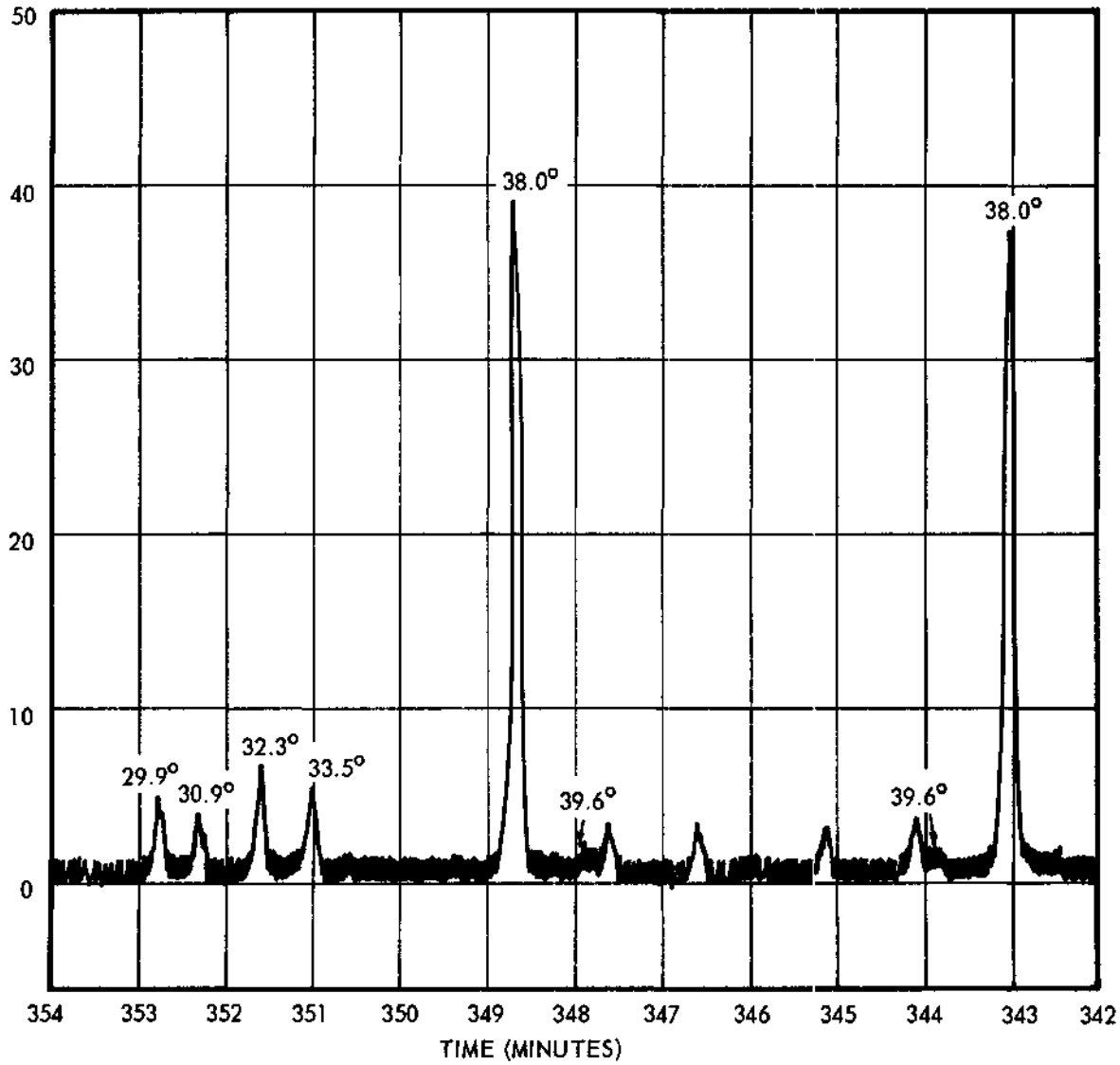

Figure A-9. Actual Diffraction Peaks of the Phases Formed in 60% Mercury Amalgams Made with Alloy C at a Given Time.

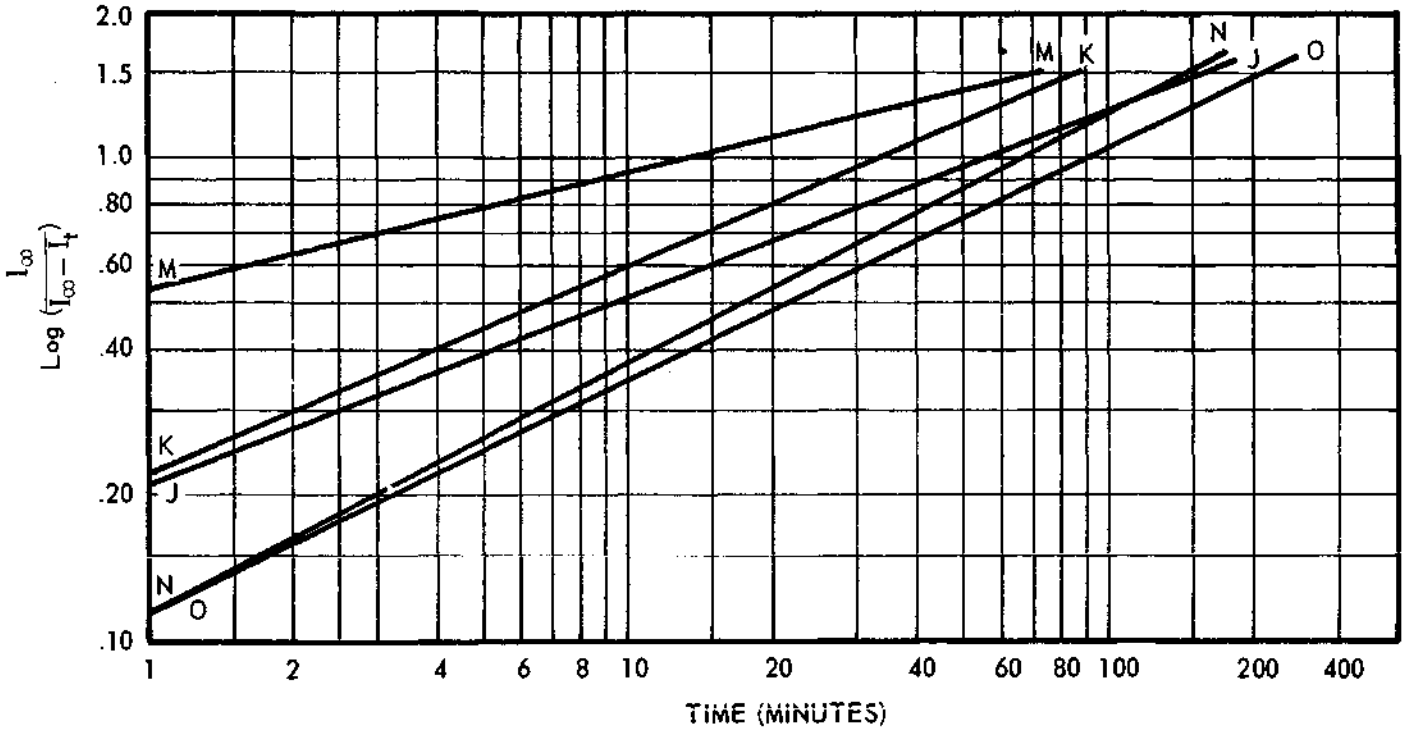

Figure A-10. Double Log of the Intensity Ratio of the Major Peak ($2\theta = 38.0^{o}$ for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 20% Mercury Amalgams Made with Commercial Alloys.

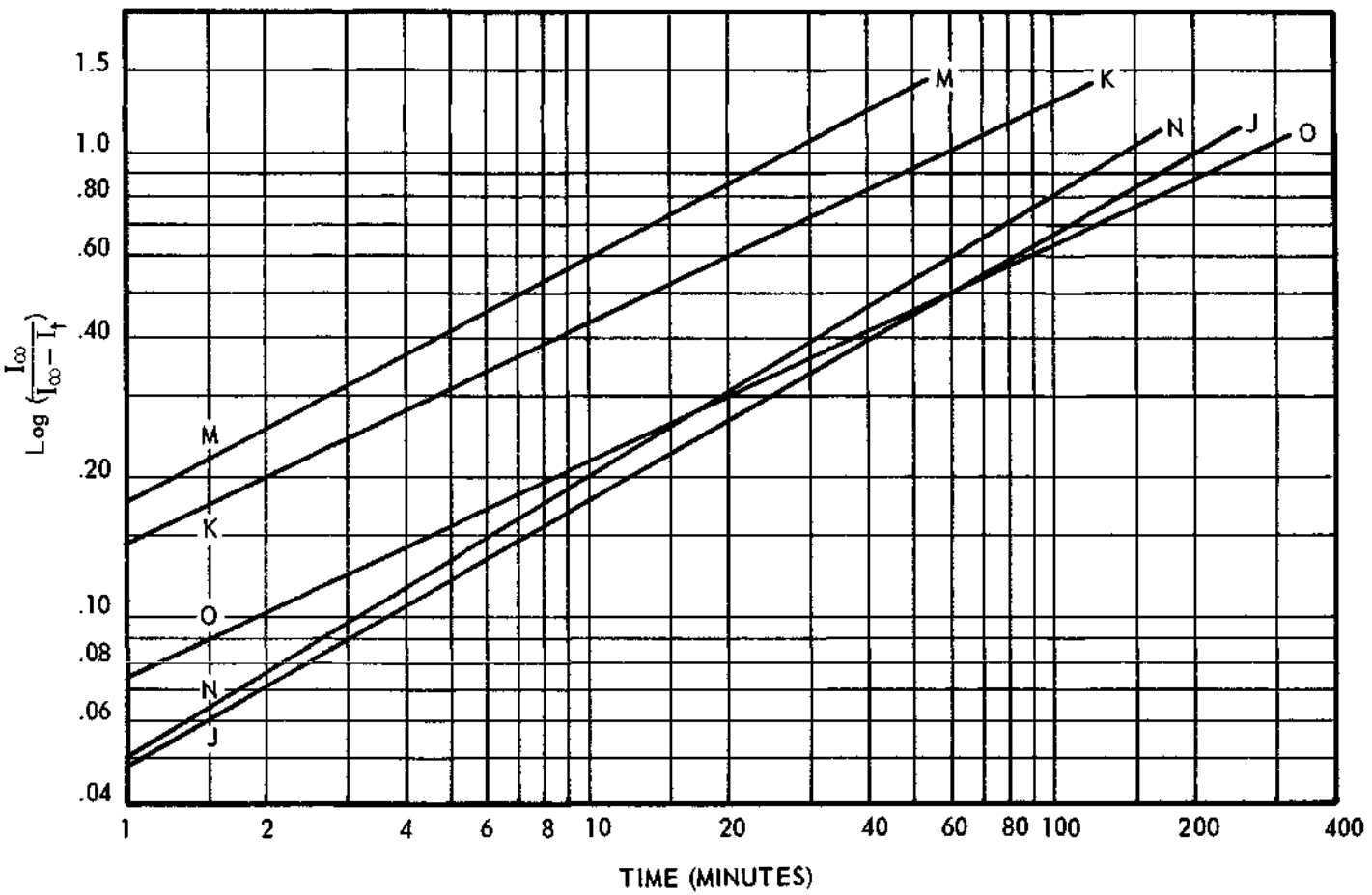

Figure A-11. Double Log of the Intensity Ratio of the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 30% Mercury Amalgams Made with Commercial Alloys.

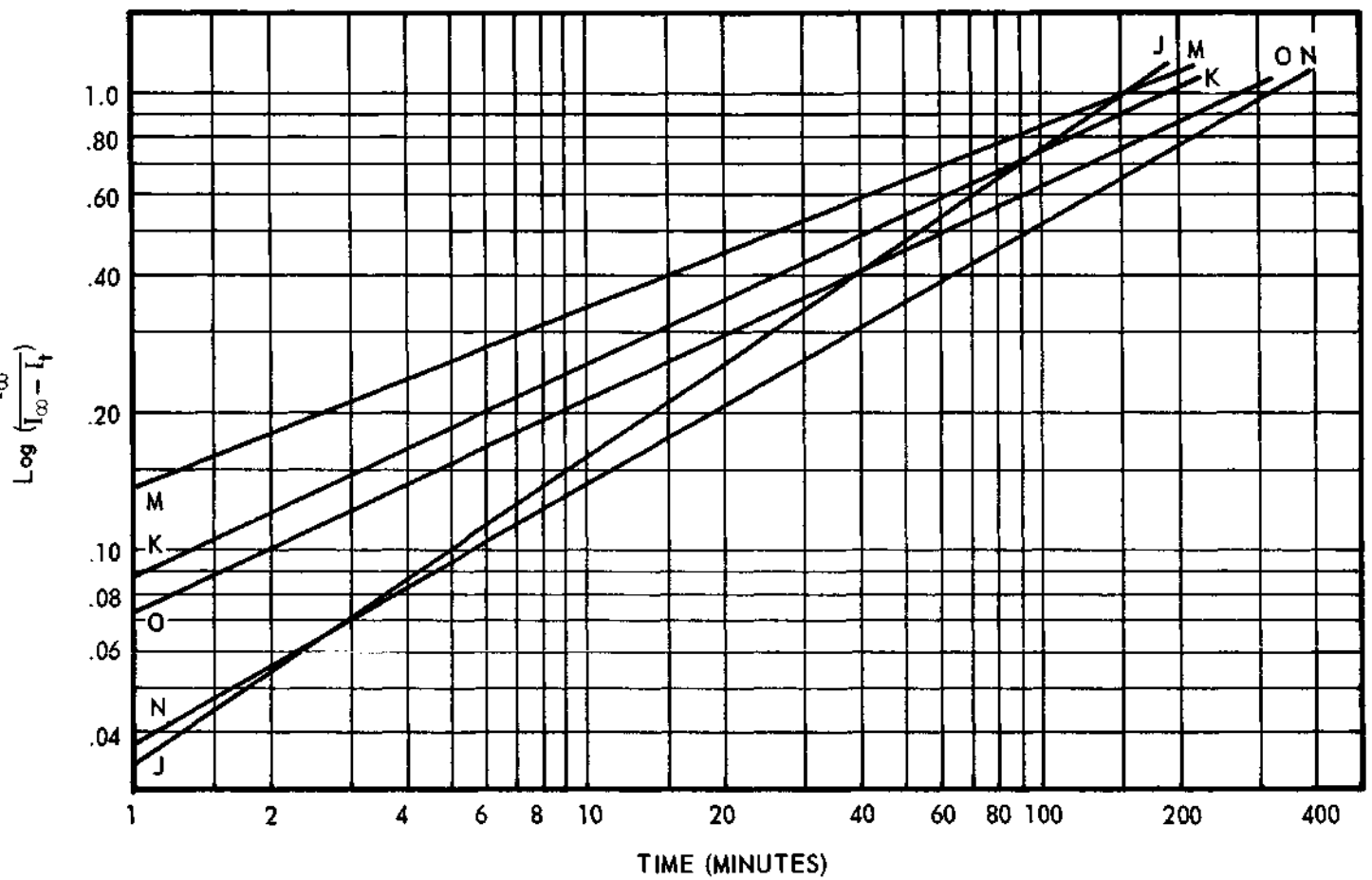

Figure A-12. Double Log of the Intensity Ratio of the Major Peak ($2\theta = 38.0^\circ$ for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 40% Mercury Amalgams Made with Commercial Alloys.

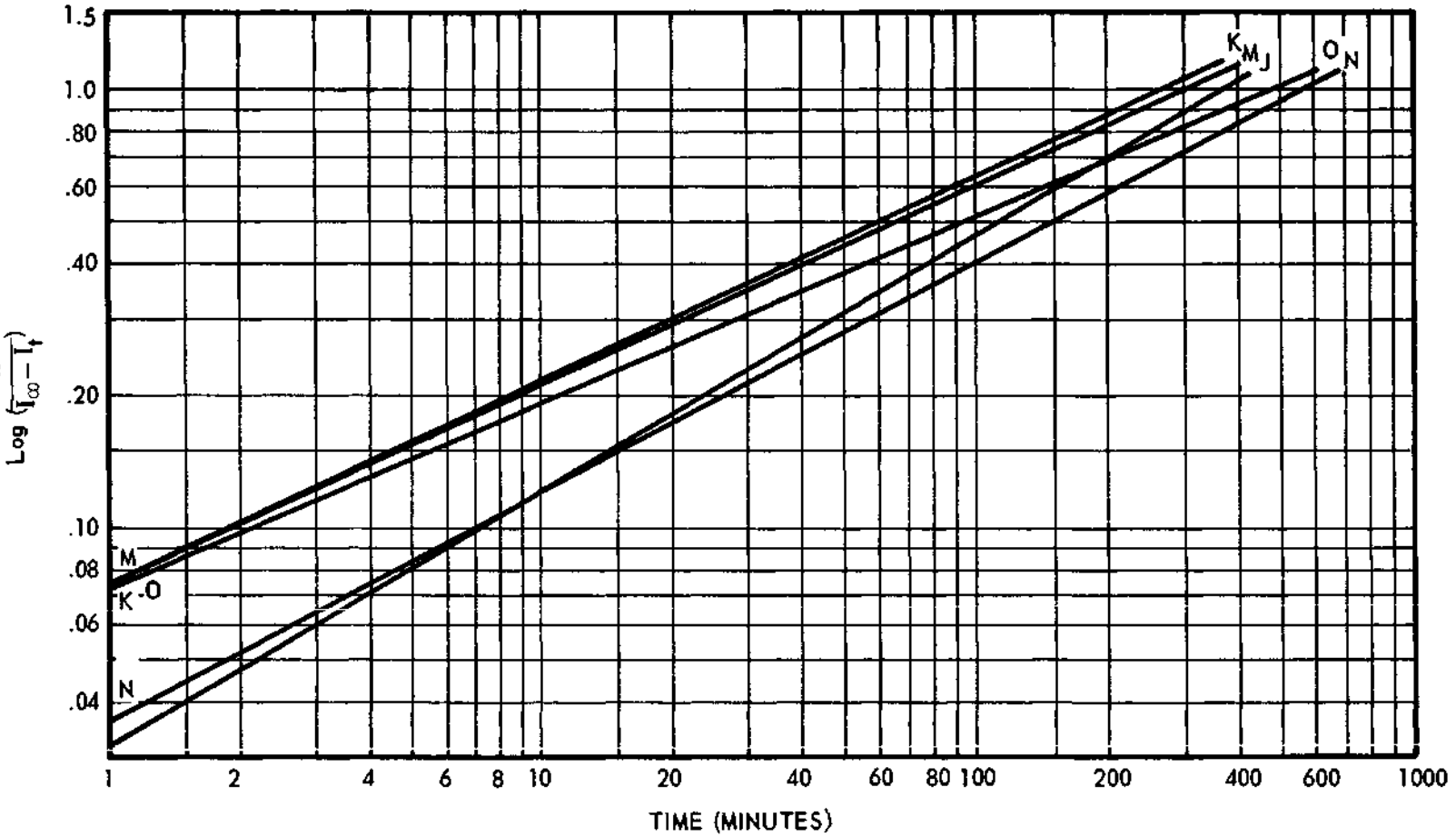

Figure A-13. Double Log of the Intensity Ratio of the Major Peak ($2\theta = 38.0^\circ$ for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 50% Mercury Amalgams Made with Commercial Alloys.

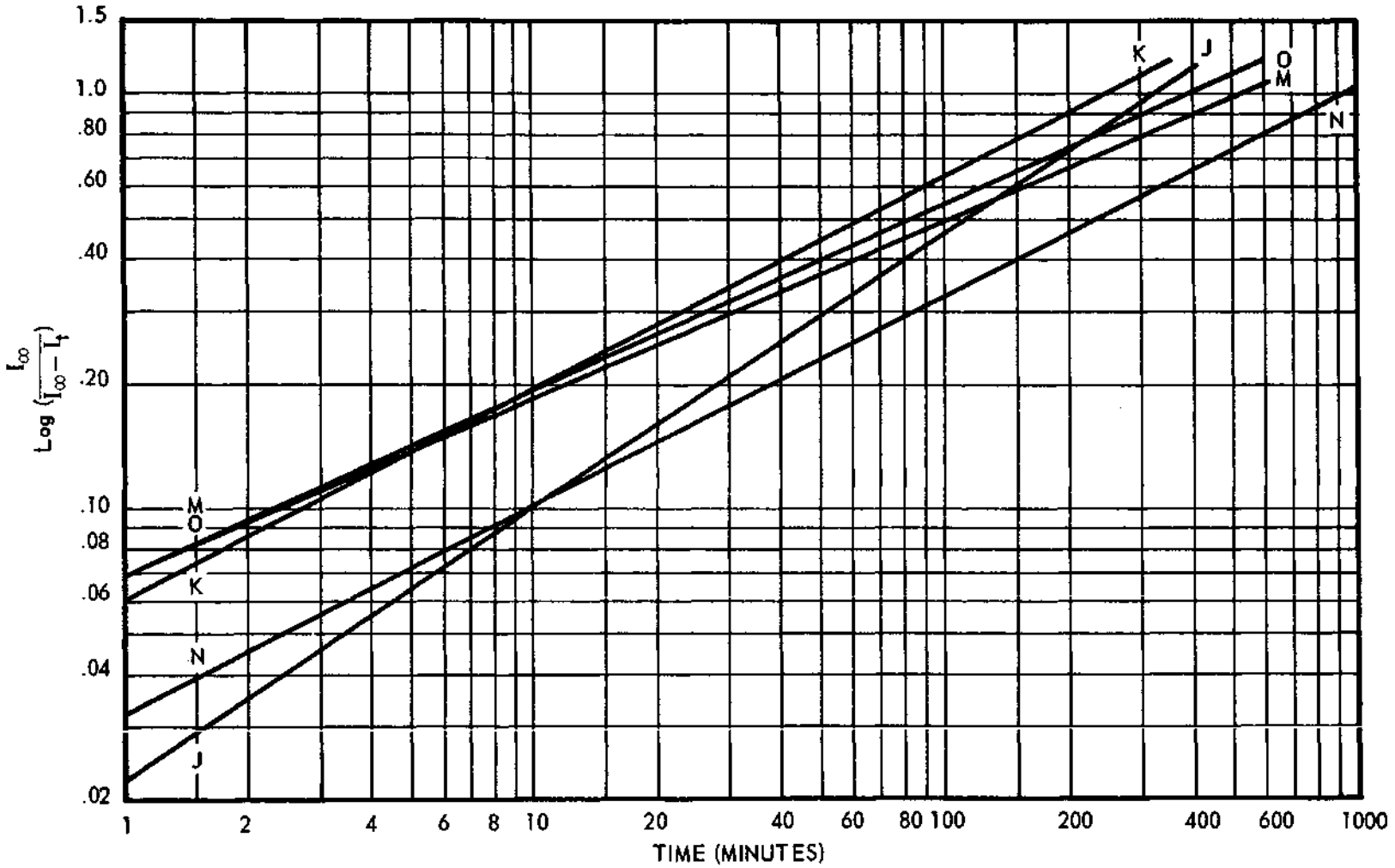

Figure A-14. Double Log of the Intensity Ratio of the Major Peak ($2\theta = 38.0^\circ$ for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 60% Mercury Amalgams Made with Commercial Alloys.

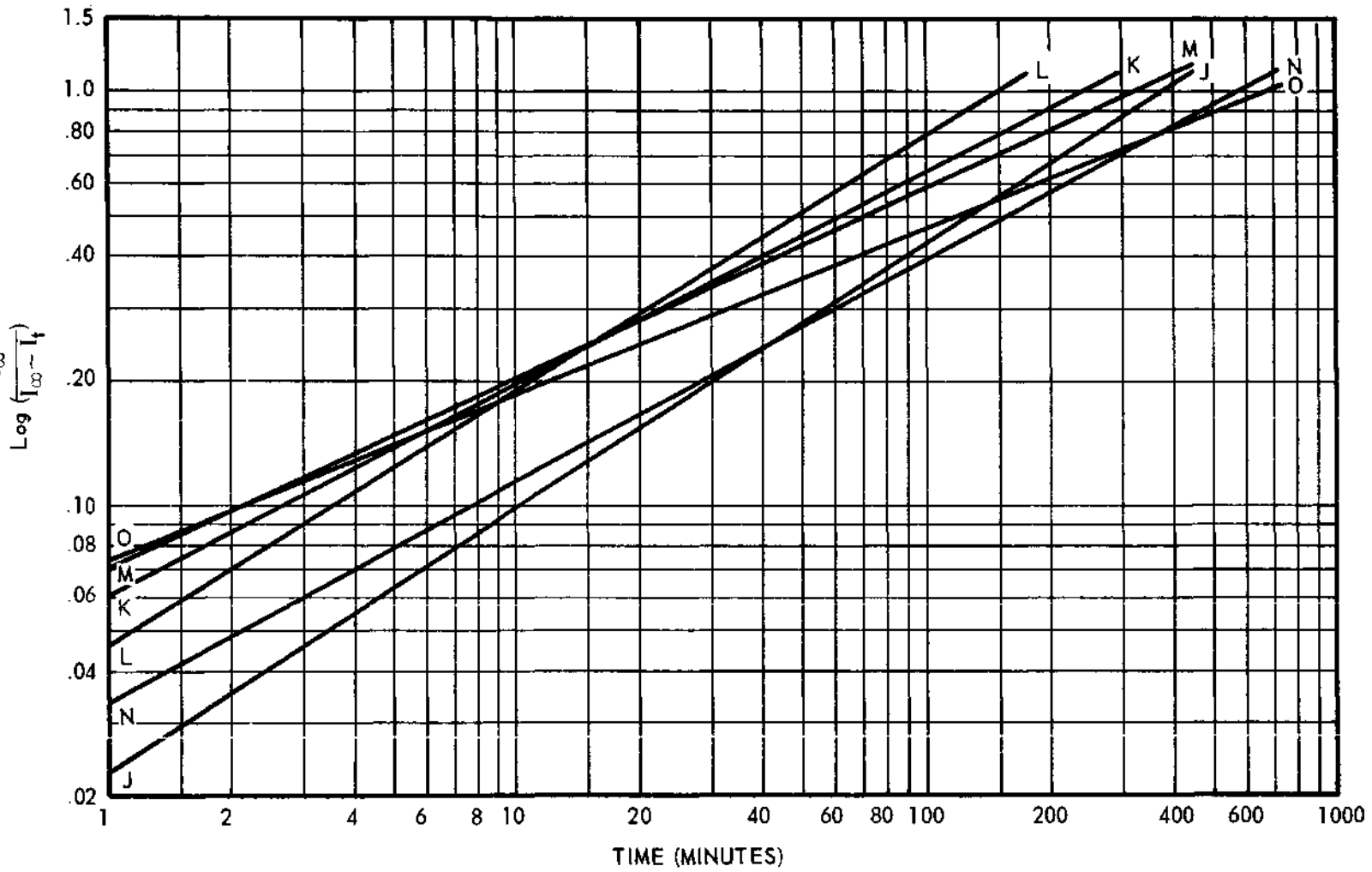

Figure A-15. Double Log of the Intensity Ratio of the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 60% Mercury Amalgams (Before Squeezing) Made with Commercial Alloys.

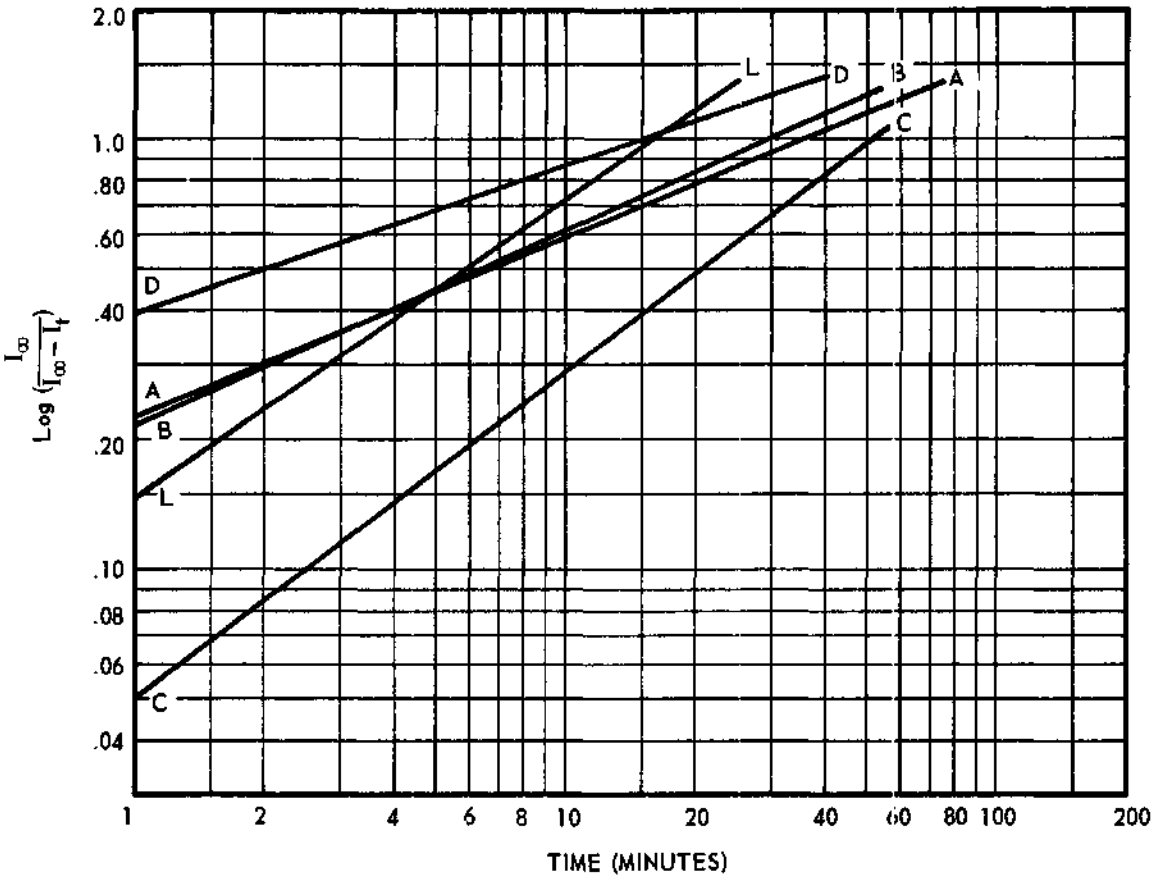

Figure A-16. Double Log of the Intensity Ratio of the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 20% Mercury Amalgams Made with Experimental Alloys.

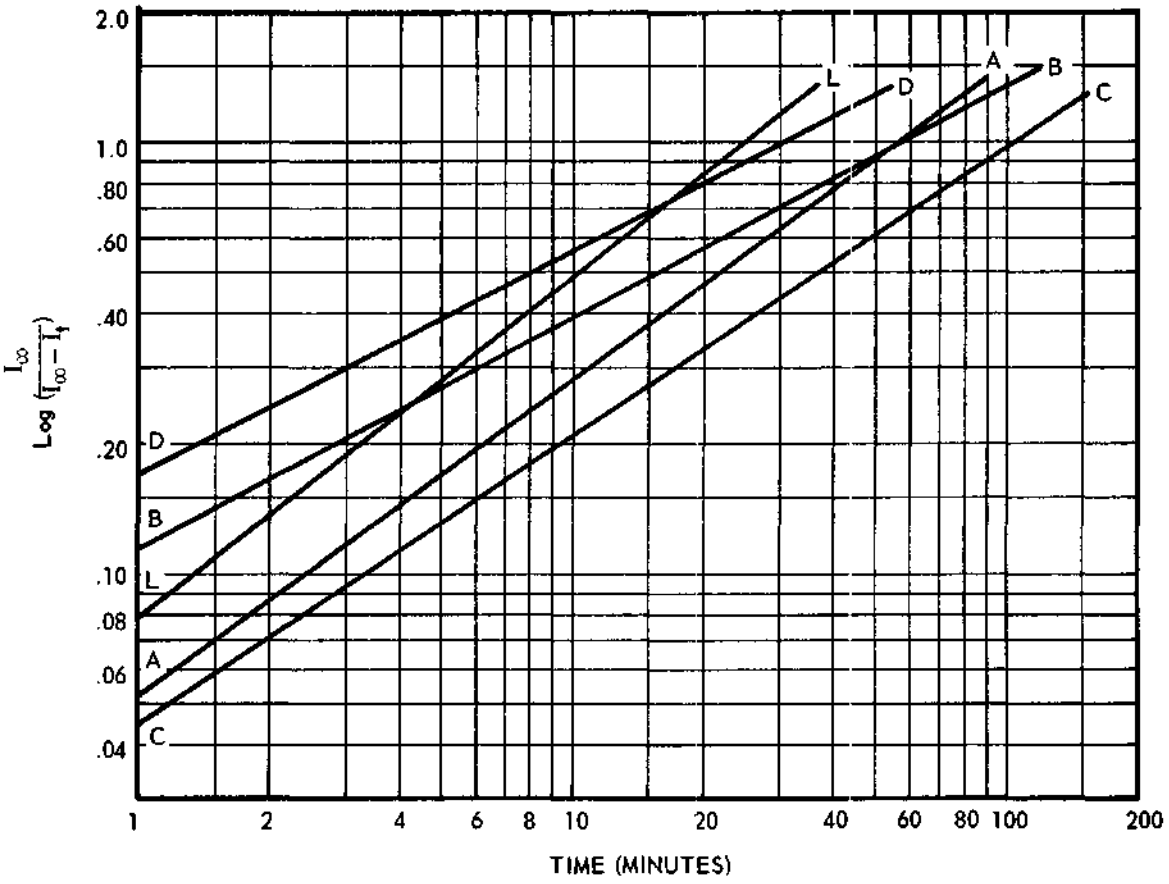

Figure A-17. Double Log of the Intensity Ratio of the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 30% Mercury Amalgams Made with Experimental Alloys.

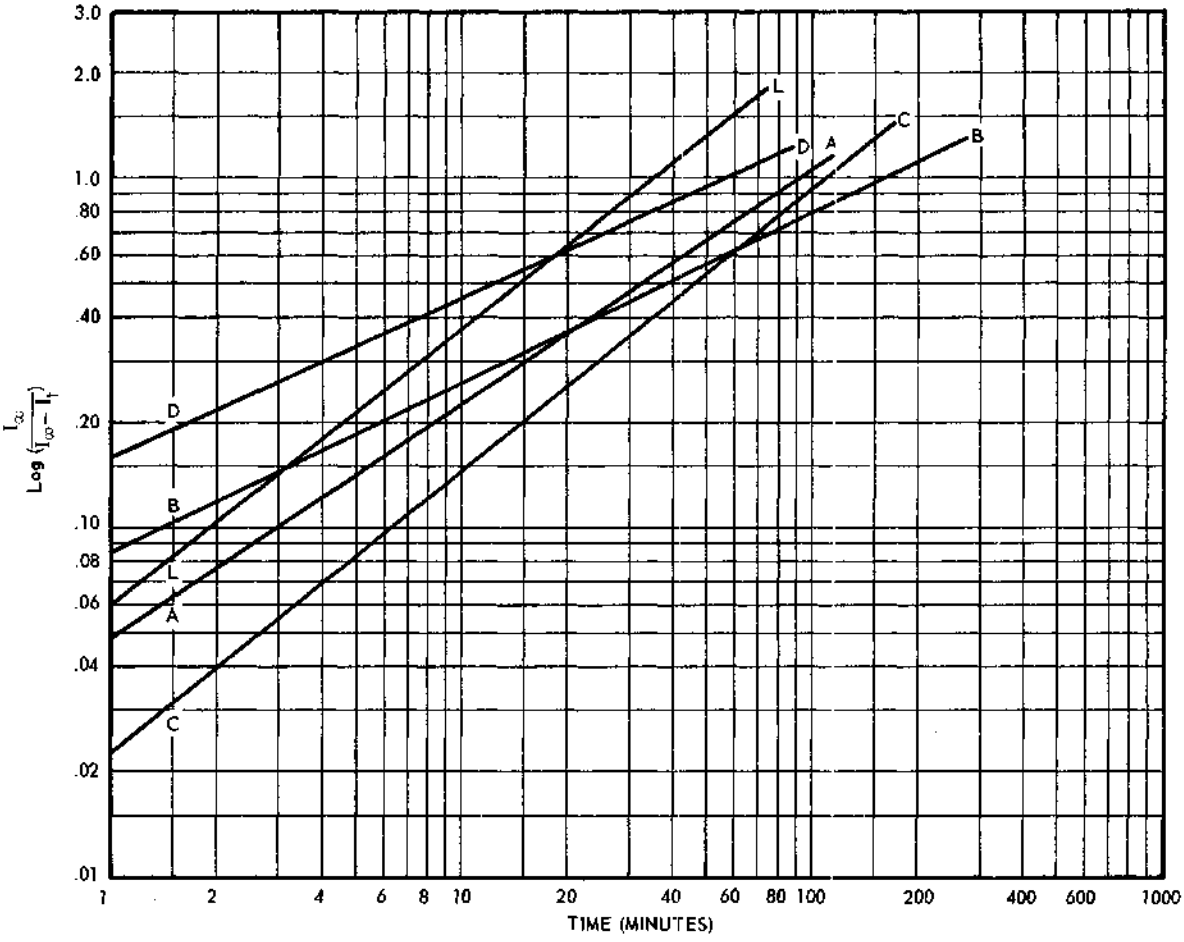

Figure A-18. Double Log of the Intensity Ratio of the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 40% Mercury Amalgams Made with Experimental Alloys.

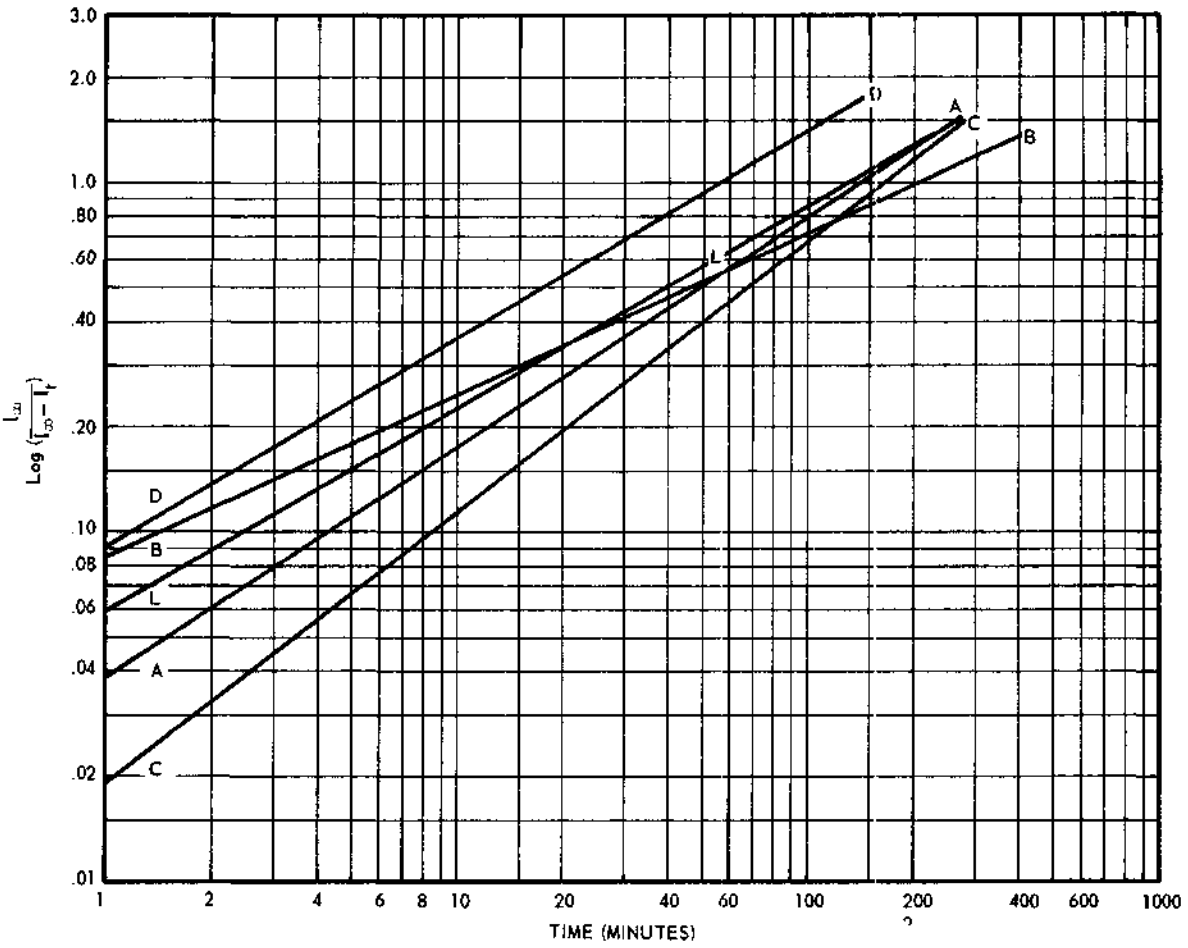

Figure A-19. Double Log of the Intensity Ratio of the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 50% Mercury Amalgams Made with Experimental Alloys.

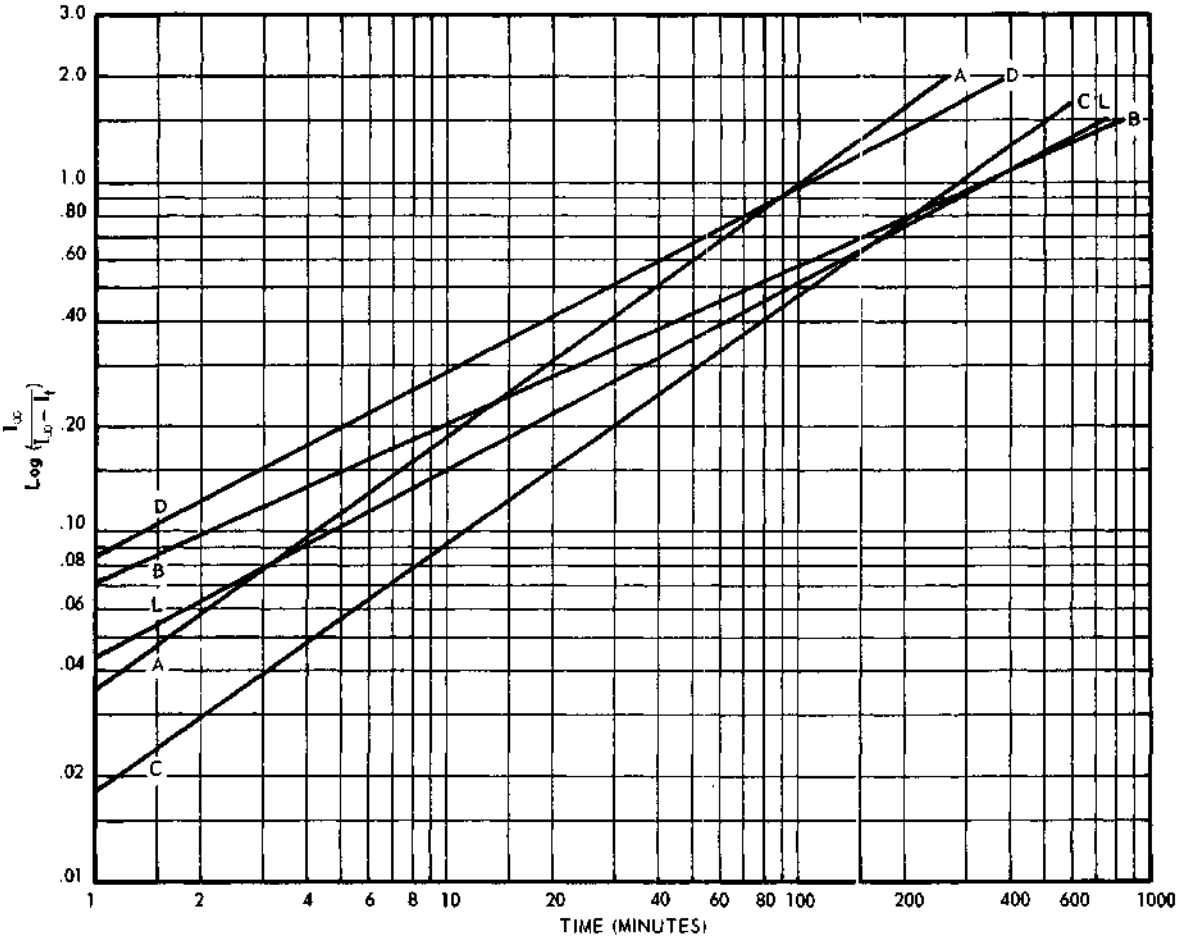

Figure A-20. Dougle Log of the Intensity Ratio cf the Major Peak (2θ = 38.0° for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for 60% Mercury Amalgams Made with Experimental Alloys.

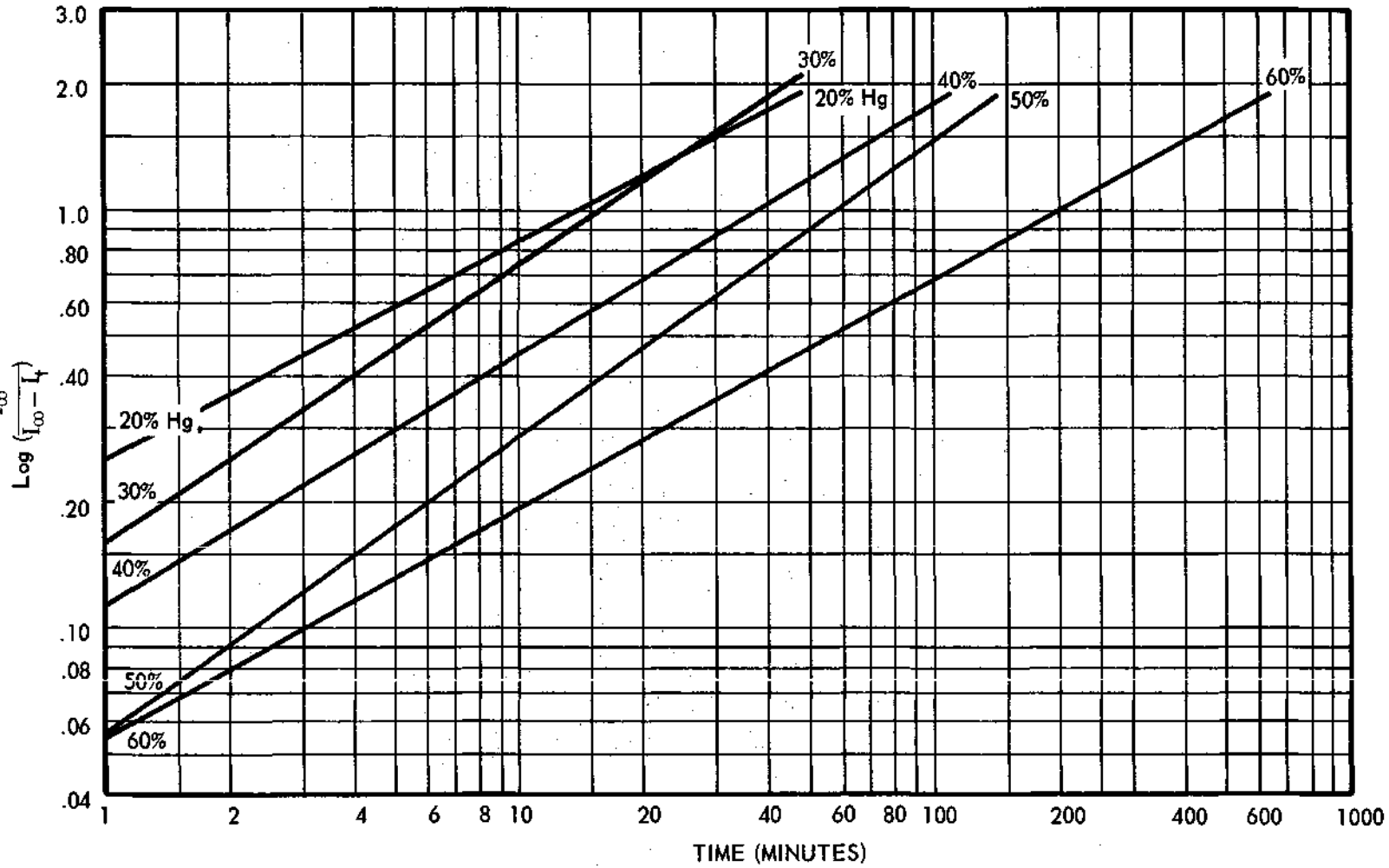

Figure A-21. Double Log of the Intensity Ratio of the Major Peak ($2\theta = 38.0^\circ$ for CuKα Radiation) of the Ag_2Hg_3 Phase versus Log Time for Amalgams Made with Spherical Alloys and Varying Amounts of Mercury.

APPENDIX B

QUANTITATIVE ANALYSIS SCHEME

APPENDIX B

QUANTITATIVE ANALYSIS SCHEME

The absorption coefficient for each phase was found using the following formula:

$$u/p = w_1(u/p)_1 + w_2(u/p)_2$$

w = weight fraction of an element within a compound

Element	MW	u/p(Cu Kα radiation)
Hg	200.61	223
Ag	107.88	223
Sn	118.70	265

for Ag_2Hg_3: $w_{Ag} = 215.76/817.59$; $w_{Hg} = 601.83/817.59$

for Ag_3Sn: $w_{Ag} = 323.64/442.34$; $w_{Sn} = 118.70/442.34$

for Sn_8Hg: $w_{Sn} = 949.60/1150.21$; $w_{Hg} = 200.61/1150.21$

Compound	u/p(Calculated)
Ag_2Hg_3	223
Ag_3Sn	233
Sn_8Hg	257

It was assumed for this work that each phase had the same absorption coefficient which simplified the calculations greatly. With this assumption, the formula to calculate the weight percent of the phase present is:

$$w_a = (I_a/I_{ap})/(I_a/I_{ap} + I_b/I_{bp} + I_c/I_{cp})$$

w_a = weight % of a phase

I_a = intensity of the major peak of the a phase in the mixture

I_{ap} = intensity of the major peak of the a phase by itself (pure)

I_b, I_{bp}, I_c, I_{cp} follow as the same for the other phases present

The same machine conditions must be used thrcughout a complete determination.

Examples:

		%	Ipure	Iin mixture	°2θ(Cu Kα)
Mixed	.3g. Ag_2Hg_3	62	35	21	38.0
	.4g. Sn_8Hg	8	150*	12	32.3
	1.5g. Ag_3Sn	30	95	30	39.6

*75 at one-half the scale factor used for the others.

$$w_{Ag_2Hg_3} = (21/35)/(21/35 + 12/150 + 30/95) = 60\%$$

$$w_{Sn_8Hg} = (12/150)/(21/35 + 12/150 + 30/95) = 8\%$$

$$w_{Ag_3Sn} = (30/95)/(21/35 + 12/150 + 30/95) = 32\%$$

This checks very well.

		%	Ipure	Iin mixture	% calculated
Mixed	4.0g. Ag_2Hg_3	84	35	31	90
	.5g. Sn_8Hg	11	150	6	5
	.25g. Ag_3Sn	5	95	4	5
	6.0g. Ag_2Hg_3	72	35	40	75
	.8g. Sn_8Hg	10	150	20	9
	1.5g. Ag_3Sn	18	95	23	16

This procedure may be tried on amalgams in bulk form, as opposed to powder, and will only be good if complete reaction has taken place or if a standard is available and if the grain sizes are equal for all phases and all samples.

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